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## INORGANIC CHEMISTRY



SCRANTON:
INTERNATIONAL TEXTBOOK COMPANY

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# PREFACE

The International Library of Technology is the outgrowth of a large and increasing demand that has arisen for the Reference Libraries of the International Correspondence Schools on the part of those who are not students of the Schools. As the volumes composing this Library are all printed from the same plates used in printing the Reference Libraries above mentioned, a few words are necessary regarding the scope and purpose of the instruction imparted to the students of—and the class of students taught by—these Schools, in order to afford a clear understanding of their salient and unique features.

The only requirement for admission to any of the courses offered by the International Correspondence Schools, is that the applicant shall be able to read the English language and to write it sufficiently well to make his written answers to the questions asked him intelligible. Each course is complete in itself, and no textbooks are required other than those prepared by the Schools for the particular course selected. The students themselves are from every class, trade, and profession and from every country; they are, almost without exception, busily engaged in some vocation, and can spare but little time for study, and that usually outside of their regular working hours. The information desired is such as can be immediately applied in practice, so that the student may be enabled to exchange his present vocation for a more congenial one, or to rise to a higher level in the one he now pursues. Furthermore, he wishes to obtain a good working knowledge of the subjects treated in the shortest time and in the most direct manner possible.

In meeting these requirements, we have produced a set of books that in many respects, and particularly in the general plan followed, are absolutely unique. In the majority of subjects treated the knowledge of mathematics required is limited to the simplest principles of arithmetic and mensuration, and in no case is any greater knowledge of mathematics needed than the simplest elementary principles of algebra, geometry, and trigonometry, with a thorough, practical acquaintance with the use of the logarithmic table. To effect this result, derivations of rules and formulas are omitted, but thorough and complete instructions are given regarding how, when, and under what circumstances any particular rule, formula, or process should be applied; and whenever possible one or more examples, such as would be likely to arise in actual practice—together with their solutions—are given to illustrate and explain its application.

In preparing these textbooks, it has been our constant endeavor to view the matter from the student's standpoint, and to try and anticipate everything that would cause him trouble. The utmost pains have been taken to avoid and correct any and all ambiguous expressions—both those due to faulty rhetoric and those due to insufficiency of statement or explanation. As the best way to make a statement, explanation, or description clear is to give a picture or a diagram in connection with it, illustrations have been used almost without limit. The illustrations have in all cases been adapted to the requirements of the text, and projections and sections or outline, partially shaded, or full-shaded perspectives have been used, according to which will best produce the desired results. Half-tones have been used rather sparingly, except in those cases where the general effect is desired rather than the actual details.

It is obvious that books prepared along the lines mentioned must not only be clear and concise beyond anything heretofore attempted, but they must also possess unequaled value for reference purposes. They not only give the maximum of information in a minimum space, but this information is so ingeniously arranged and correlated, and the

indexes are so full and complete, that it can at once be made available to the reader. The numerous examples and explanatory remarks, together with the absence of long demonstrations and abstruse mathematical calculations, are of great assistance in helping one to select the proper formula, method, or process and in teaching him how and when it should be used.

The numerous questions and examples, with their answers and solutions, which have been placed at the end of each volume, will prove of great assistance to all who consult the Library.

In the present volume, the entire field of inorganic chemistry has been covered as thoroughly as is necessary to meet the wants of the working chemist. The lately discovered gaseous elements have been omitted, as they are of no practical value at present and are not likely to be in the future. On the other hand, the greatest care has been taken to treat as fully as possible all those elements and inorganic compounds that are in daily use in the arts and manufactures and in chemical analysis. The work should prove of great value to all interested in chemistry and especially to manufacturing and analytical chemists.

The method of numbering the pages, cuts, articles, etc. is such that each subject or part, when the subject is divided into two or more parts, is complete in itself; hence, in order to make the index intelligible, it was necessary to give each subject or part a number. This number is placed at the top of each page, on the headline, opposite the page number; and to distinguish it from the page number it is preceded by the printer's section mark (§). Consequently, a reference such as § 16, page 26, will be readily found by looking along the inside edges of the headlines until § 16 is found, and then through § 16 until page 26 is found.

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CONTENTS.

# INORGANIC CHEMISTRY.

(PART 1.)

## NON-METALS OR METALLOIDS.

### HYDROGEN.

*Symbol H. Atomic weight 1. Density 1. Valence I. Specific gravity .0693. Molecular weight 2. One liter weighs .0896 gram (1 crith).*

**1. History.**—Hydrogen was discovered by Paracelsus in the 16th century. In the year 1766, Cavendish, an English chemist, investigated this gas more thoroughly, and gave it the name of *inflammable air*, and, by continued investigations, he proved, in 1781, its elementary character. Lavoisier finally gave it the name of *hydrogen*.

**2. Occurrence.**—Hydrogen occurs, to a certain extent, uncombined in nature. It is found in a number of volcanic gases. Bunsen, for instance, found that it formed nearly 45 per cent. of the gaseous exhalations of Nimarfjall, in Iceland. Spectrum analysis further showed hydrogen to be a free constituent of the sun, as well as of certain fixed stars and nebulæ. Graham obtained from the Lenarto meteorite—an exceptionally pure iron—three times its own volume of hydrogen. The chief source of hydrogen is water, a compound that consists of 8 parts of oxygen combined with 1 part

of hydrogen; it is also met with in *petroleum*, *bitumen*, and *all animal* and *vegetable tissues*.

**3. Preparation.**—The attraction of the metals *sodium* and *potassium* for oxygen is so great that they readily decompose water, thus liberating the hydrogen it contains, which, with sufficient care, may be easily collected.

EXPERIMENT 1.—Drop a very small piece of sodium, about half the size of a small pea, into a basin filled with water; note that it melts, and, rushing around on the surface for some time, becomes smaller and smaller and finally disappears.

Next, place a piece of either filter paper or blotting paper on the surface of the water, and drop a fragment of sodium on the paper. It soon melts, and then takes fire, burning with an intensely yellow flame.

Drop a piece of potassium, about the same size as the piece of sodium, in water; it at once takes fire and burns with a flame of a characteristic violet hue. (In this case the use of filter paper is unnecessary.)

The combination of sodium and potassium with oxygen, under these circumstances, is accompanied with considerable heat, which inflames the hydrogen gas liberated from the water by the action of the metal. It is this gas that produces the flame; the characteristic tint in each case is due to the presence of the vapor of each metal.

In any of these experiments with sodium or potassium and water, in which the escaping gas should take fire, stand some little distance off until it has burned out, and then wait until the molten hydrate, which first floats on the surface of the water, is dissolved; *at this moment there is always a slight spit, and there is danger, if you are standing immediately over it, that portions of the flying hydrate may get in your eye and hurt it seriously.*

It would be advisable for the student to omit these experiments for the present, and satisfy himself with carefully reading and studying them.

If the fragment of metal, instead of being allowed to float on the water, is held under the surface of it by means of a pair of forceps, bubbles of gas are seen to rise; these consist of hydrogen, and may be collected in the following manner: Fold a piece of wire gauze in a cone, in exactly the same way as directed to fold filter paper in Art. **99,** *Theoretical*

*Chemistry.* Have a pair of tongs by which you can hold this cone point upwards under the water. Place in the water basin a glass jar, inverted and full of water, ready for collecting the gas; be quite sure that *not one* bubble of air remains in the jar; that is, fill the jar with water till it overflows, close the mouth with a piece of plate glass, and quickly turn it upside down, immersing the mouth of the jar in the water of the basin; then remove, while thus submerged, the glass plate, and rest the jar's mouth on the bottom of the basin. Throw a piece of sodium, about the size of a pea, in the water of the basin, and at once depress it beneath the surface, with the gauze cone held in the tongs like a candle extinguisher; the point of the cone must be at least half an inch below the surface of the water. Wait until after the first bubbles of gas have risen; then hold the jar, without lifting it out of the water, over the point of the cone under which the sodium is decomposing the water, and collect the rising bubbles. Repeat this operation with a fresh piece of sodium, if necessary, until the jar is filled; that is, until all the water it contained has been driven out, or *displaced*, by the evolved hydrogen. Then lift the jar out of the basin, mouth downwards, and apply a lighted match to the gas in the jar; you will notice that it burns with a peculiar pale flame, tinged with yellow. This yellow hue is due to the sodium vapors that have been collected, incidentally, with the hydrogen.

The chemical reaction, representing the evolution of hydrogen, may be expressed thus:

$$\underset{\text{sodium}}{Na_2} + \underset{\text{water}}{2H_2O} = \underset{\text{sodium hydrate}}{2NaHO} + \underset{\text{hydrogen}}{H_2}$$

EXPERIMENT 2.—Take another small fragment of sodium, and dissolve it by throwing it in a small quantity of water in an evaporating basin; when the action is over, observe the soapy feeling that the water now possesses and imparts to your fingers; this is characteristic of the class of bodies of which sodium hydrate, which has been formed according to the equation given above, is a member. Evaporate the water by placing the basin on a tripod, protecting the basin from cracking by first placing a piece of wire gauze on the tripod, and applying

heat; notice that, after the water has evaporated, a white, solid substance is left behind.

*Sodium hydrate*, popularly known as *caustic soda*, or *soda lye*, shows by its formula that it contains 1 atom of hydrogen; it may, in fact, be regarded as water in which one of the atoms of hydrogen has been replaced by 1 atom of sodium.

We are also able to replace the second atom of hydrogen by zinc, or, still better, by aluminum, forming sodium aluminate.

EXPERIMENT 3.—Fit a small flask with a stopper and delivery tube; place in it a few strips of aluminum and a piece of sodium hydrate, and add just sufficient water to cover the bottom of the flask. Fix in the retort stand and apply heat (see Fig. 1). At first, bubbles of air

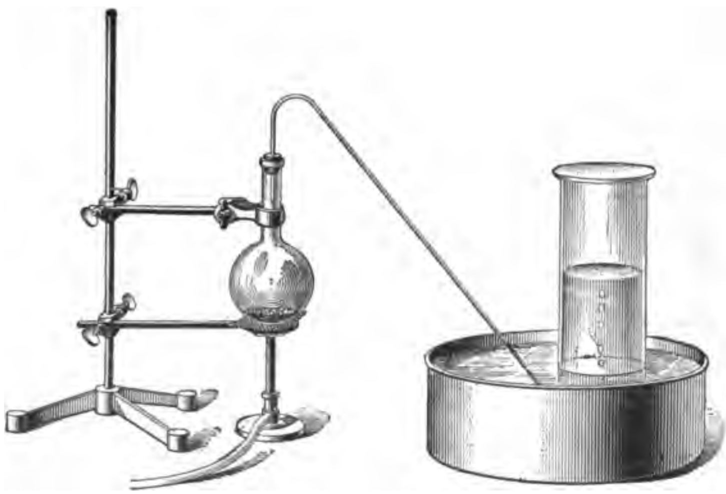

FIG. 1.

come over, but as soon as the air is expelled from the apparatus, hydrogen may be collected over the pneumatic trough.

The water takes no part in the reaction, but is simply added to prevent the heat from cracking the flask, and to dissolve the sodium hydrate, thus promoting chemical action.

The following is the reaction that occurs:

$$\underset{\text{sodium hydrate}}{6NaOH} + \underset{\text{aluminum}}{Al_2} = \underset{\text{sodium aluminate}}{2Na_3AlO_3} + \underset{\text{hydrogen}}{3H_2}$$

If the direction is given to collect a gas over the pneumatic trough, it is meant that the gas has to be collected under water. For this purpose a large basin, or pan, is half filled with water, the beehive shelf (see Fig. 2) is placed in the pan, and the delivery tube led into the side opening of the shelf; the jar in which the gas is to be collected is filled with water, inverted, and placed over the top opening of the beehive shelf (see Fig. 3).

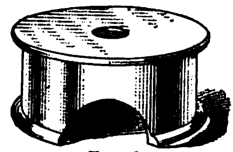

FIG. 2.

The most interesting feature of these experiments is that, by means of them, we succeed in obtaining hydrogen from

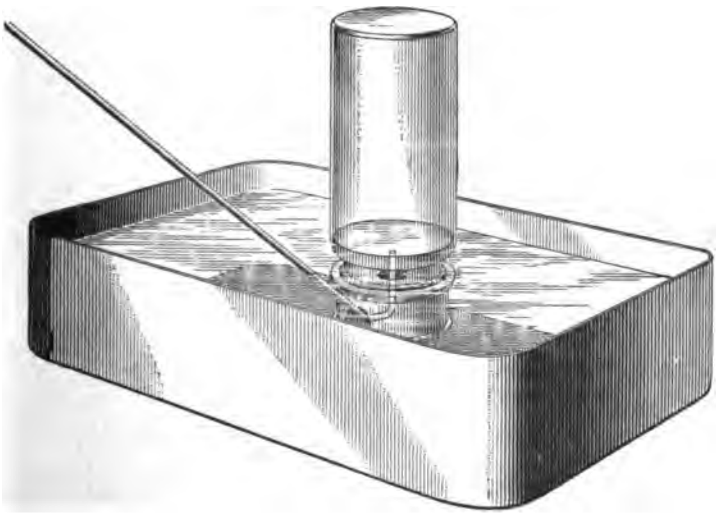

FIG. 3.

water in two distinct instalments, proving that at least two atoms of hydrogen are present in the molecule of water. Making use of an atomic instead of a molecular equation, the two successive displacements of hydrogen may be thus represented:

$$(1)\qquad \underset{\text{water}}{HHO} + \underset{\text{sodium}}{Na} = \underset{\text{sodium hydrate}}{NaHO} + \underset{\text{hydrogen}}{H}$$

(2) $\underset{\text{sodium hydrate}}{3NaOH} + \underset{\text{aluminum}}{Al} = \underset{\text{sodium aluminate}}{Na_3AlO_3} + \underset{\text{hydrogen}}{3H}$

Written in this manner, the replacement of the hydrogen in two steps is shown very clearly.

The most convenient method of preparing hydrogen consists of acting on either granulated zinc or iron with diluted sulphuric or hydrochloric acid. As a rule, zinc and sulphuric acid are employed. The gas comes off readily at the ordinary temperature.

$$\underset{\text{zinc}}{Zn} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{zinc sulphate}}{ZnSO_4} + \underset{\text{hydrogen}}{H_2}$$

Experiment 4.—(This experiment should be performed by the student.)

The granulated zinc, about half an ounce, is placed in a wide-mouthed bottle (see Fig. 4) having two holes through the cork that

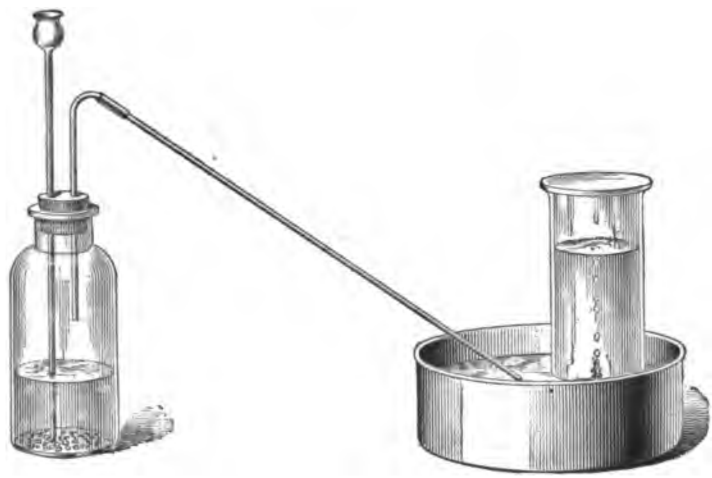

Fig. 4.

closes it. Through one of these openings a funnel tube passes to the bottom of the bottle, and through the other a delivery tube to the pneumatic trough, terminating, after passing through the beehive shelf, beneath an inverted cylinder or jar filled with water, which rests on the beehive shelf, as has been shown in Fig. 3. On pouring diluted sulphuric acid (1 part of the commercial acid and 6 parts of water, and

cooled by placing the glass containing the acid solution in a basin filled with cold water) through the funnel tube upon the zinc, effervescence occurs, and bubbles escape from the delivery tube. Do not, however, add much acid at a time; one teaspoonful at a time is quite sufficient, otherwise the action will become too violent, and the mixture will become too hot and froth through the funnel tube; should there be any indication of this, pour a little water into and also on the outside of the flask, in order to cool it.

Care should be taken that all the air is expelled from the flask and glass tubing before the hydrogen can be collected. It is, therefore, recommended *not* to place the collection jar in its place until all the air is driven out by the evolved hydrogen. This is easily ascertained by filling, in the already described way, a small test tube with the gas, and by trying whether it burns quietly when a light is brought close to the mouth of it. (The tube must, owing to the lightness of hydrogen, be held with the mouth downwards.) If all the air has been expelled from the apparatus, the gas will burn quietly; if not, it will ignite with a slight detonation.

**4. Properties** (*Physical*).—Hydrogen is a colorless, odorless, and tasteless gas, and is the lightest substance known to exist. It is 14.43 times lighter than air, 11,000 times lighter than water, and 240,000 times lighter than platinum. Hydrogen is very slightly soluble in water, 100 volumes dissolving only 1.93 volumes of the gas. Hydrogen is used as the standard of density, molecular weight, and volume of gases and vapor.

Hydrogen passes with great ease through animal and vegetable membranes, as well as through porous substances that are impervious to water. It cannot be preserved in any vessel having the slightest crack or flaw, for it would pass through it with a much greater readiness than air. This property is expressed by saying that hydrogen is very *diffusible*. Hydrogen, in many ways, behaves as a metal; it is, for instance, the only gas that shows a noticeable property of conductivity of heat, and it has, consequently, been repeatedly proposed to class it among the metals.

In order to liquefy a gas, it becomes necessary that its molecules shall manifest a certain degree of cohesion, or, in other words, that the amplitude of molecular movement shall be arrested as far as possible. This amplitude of

molecular movement depends, more or less, on the temperature to which the gas is subjected, from which it follows that for every known gas there is a certain temperature above which liquefaction cannot take place, regardless of the pressure applied to the gas. This temperature is known as the *critical temperature*. The critical temperature of hydrogen is about $-180°$, which means that at or below this temperature hydrogen may be obtained in the liquid state by subjecting it to pressure. About 99 atmospheres pressure would probably be required at this temperature, but if the temperature is still further depressed, less pressure will be required. By subjecting hydrogen to pressure at very low temperatures, two chemists, MM. Cailletet and Pictet, have succeeded in liquefying it.

Among other physical properties possessed by hydrogen must be mentioned its remarkable faculty of passing through plates of iron and platinum at elevated temperatures. According to Graham, who thoroughly investigated this phenomenon, this faculty is closely related to the property possessed by a number of solid bodies, and particularly metals, such as platinum, iron, and palladium, of absorbing hydrogen. Graham designated this phenomenon by the name of *occlusion* of hydrogen by the metals. Palladium, especially, is distinguished by its energy to absorb, or *occlude*, hydrogen. It is capable of taking up over 900 times its own volume of hydrogen at ordinary temperatures, forming a white, metallic solid, containing its constituents in ratios nearly atomic.

Graham's investigations on this subject led him to believe that the hydrogen in this substance is a solid metal with a density of about 2, and analogous, in many ways, to magnesium; that further it possesses a certain amount of tenacity, as well as the ability to conduct electricity; and that it is, to a certain extent, magnetic. He therefore proposed for this substance the name of *hydrogenium*.

**5. Properties** (*Chemical*).—Hydrogen is a combustible gas which, when heated to 500°, becomes capable of uniting

with the oxygen of the air, with the evolution of light and heat. It burns with a non-luminous and almost colorless flame at ordinary pressure, but its luminant power is increased as the atmospheric pressure is increased. Though non-luminous at ordinary temperatures, its flame evolves a great amount of heat; that is, 1 gram of burning hydrogen is able to raise the temperature of 34,462 grams of water from 0° to 1°, or, in other words, the hydrogen flame produces 34,462 units of heat.

Hydrogen is combustible, but not a supporter of combustion; a lighted candle plunged into a jar filled with hydrogen is at once extinguished. It does not support respiration—animals losing life when confined in it; it should, however, not be assumed from this fact that the gas is poisonous; the cause of death is simply a deprivation of the oxygen necessary to animal life.

Hydrogen is chosen as the standard of atomic weight and of valence.

Water is the sole product of the combustion of hydrogen in atmospheric air or oxygen; whence, as already stated, the name *hydrogen*—derived from two Greek words meaning "water producer"—was given to it by Lavoisier.

$$2H_2 + O_2 = 2H_2O.$$

As all gases obtained from mixtures in which water is present contain a certain quantity of aqueous vapor, it is necessary to dry the hydrogen before attempting to prove the presence of water as a result of its combustion. This is accomplished by passing the gas to be dried over some substance possessing a strong affinity for water. The most important *desiccating*, or *drying*, *agents* used in the laboratory are *calcium chloride*, *quicklime*, and *sulphuric acid*. Whichever of these is the most suitable depends, of course, on the nature and properties of the gas to be dried. Hydrogen, for instance, may be dried by passing through either calcium chloride or sulphuric acid.

EXPERIMENT 5.—(*If the student should attempt to perform this experiment, great care should be taken to avoid an explosion, and he should take great pains to follow all the directions minutely.*)

Choose a piece of glass tubing of about half-an-inch bore and about 10 inches long, and fit a cork to each end. To one cork fit a tube bent at right angles, with the end drawn out to a fine point, so as to form a jet; through the other pass a piece of tubing bent to the shape shown in Fig. 5, and attach to the hydrogen-generating flask *A*. Fill the large tube with small pieces of calcium chloride, and place at each end, between the chloride and the cork, a plug of cotton wool. A slow current of gas passed through this apparatus will emerge in the dry state. Let the gas escape until a test tube collected burns quietly without explosion; then attach the drying tube *B*, and after a few seconds light the gas as it issues from the jet.


FIG. 5.

Take a glass tube *C*, about 15 to 18 inches long and about ½ inch in diameter; dry the inside by pushing a plug of cotton wool through; hold it over the burning jet; the watery vapor produced by the ignition of hydrogen in air condenses in the cooler parts of the tube.

*Too much stress cannot be laid on this injunction: to* **first** *see,* **before** *lighting the jet, that a collected test tube of the gas burns quietly. Want of attention to this direction will lead to the* **explosion** *of the whole apparatus.*

This experiment is often accompanied by a peculiar musical note, produced by a rapid series of small explosions within the long tube. The moisture that condenses on a kettle, or other vessel filled with cold water and heated over a gas flame, is the product of combustion of the hydrogen of the coal gas.

Hydrogen is the lightest substance known, and for this reason is used for the purpose of filling balloons. The amount a balloon will carry, that is, its ascensional power, is the difference between the weight of the balloon itself with its contained hydrogen, and the weight of an equal volume of air. One liter of hydrogen possesses an ascensional force

of 1.2 grams. The following experiment is illustrative of this property:

EXPERIMENT 6.—Take a jar of hydrogen, and, setting it down mouth upwards, take off the glass cover; after the expiration of about half a minute, apply a match; the gas will be found to have entirely escaped. Take a second jar, and, holding it mouth downwards, remove the closing glass cover; let it also remain about a half minute and apply a light; the gas will burn as usual, but little of it having escaped.

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### SUMMARY.

**6.** Hydrogen is principally found in water. It may be prepared by the action of certain metals on that liquid, as, for example, by sodium or potassium; also, by the action of zinc or iron on acids.

Hydrogen is a colorless, tasteless, and odorless gas, inflammable, and a non-supporter of respiration or combustion. It is the lightest body known.

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### LABORATORY DIRECTIONS.

**7.** It must not be forgotten, in dealing with sodium or potassium, that the fingers and forceps must be **perfectly dry.**

In collecting hydrogen from sodium hydrate and aluminum (Experiment 3), if the neck of the flask has been touched with the soda there is frequently some difficulty in keeping the cork in its place, from its consequent soapiness. This may, as a rule, be prevented by just touching the cork all round with diluted sulphuric acid.

Great care should be taken in diluting sulphuric acid; on **no account add water to sulphuric acid.** In diluting sulphuric acid, *add the acid to the water* in very small proportions very slowly (drop by drop).

Never omit the precautionary measures previously given before lighting a jet of hydrogen.

In handling chloride of calcium, place it in the drying tube as quickly as possible; do not expose it unnecessarily to the air, and replace the cork *immediately* in the bottle containing it.

The Experiments 1, 2, 3, and 5 are usually confined to the lecture table. Study the apparatus, general arrangements, and results carefully.

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## OXYGEN.

*Symbol O. Atomic weight 15.96. Density 15.96. Valence II. Specific gravity 1.1056. Molecular weight 31.92. One liter weighs 1.429 grams (15.96 criths).*

**8. History.**—Dr. Priestley, of Birmingham, Eng., discovered, in 1774, that by heating mercury in contact with air in a closed vessel the amount of air present was lessened, and that red scales were formed on the surface of the mercury;

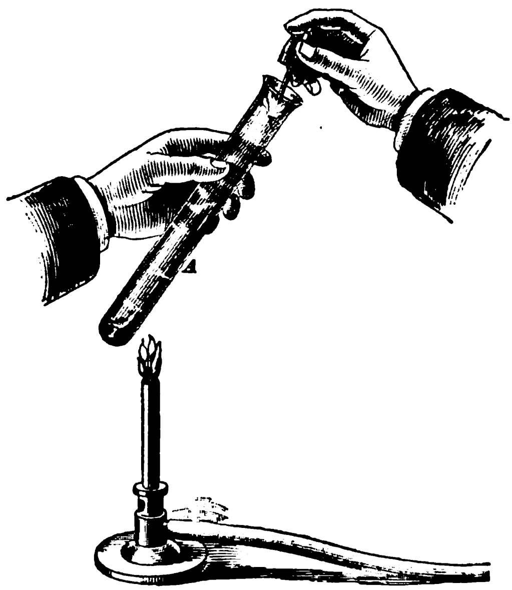


FIG. 6.

he found that the red scales thus produced consisted of mercury and a gas which he named *dephlogisticated air.* The following year, 1775, Scheele, a Swedish chemist, discovered, independently, the same gas, which he named *empyreal air.*

Condorcet called it *vital air*, till, in 1781, Lavoisier named it *oxygen*, from the Greek words for *acid former*.

**9. Occurrence.**—Oxygen is the most abundantly occurring gas in nature; it exists free in the air, of which it forms about one-fifth. Combined with other elements, it constitutes two-thirds of the entire globe. Water alone consists of eight-ninths of oxygen; and fully one-half of the weight of all minerals, three-quarters of the weight of all living beings, and nearly four-fifths, by weight, of all plants is oxygen.

**10. Preparation.**—EXPERIMENT 7.—A small quantity of mercuric oxide is heated in a test tube (*A*, Fig. 6). Presently the tube becomes lined with a mirror of metallic mercury, which after a little while separates into little drops; and if a match or wax taper, previously lighted and extinguished, but still bearing a spark at the end, be thrust into the mouth of the tube, it instantly bursts into flame and burns with great brilliancy.

This effect is due to a gas which is being disengaged, and which, to use Lavoisier's own expression, is "*eminently fitted to support combustion.*" In other words, it is oxygen, which is produced by a very simple reaction; that is, the mercuric oxide has been decomposed by heat into mercury and oxygen, according to the equation:

$$\underset{\text{mercuric oxide}}{2HgO} = \underset{\text{mercury}}{2Hg} + \underset{\text{oxygen}}{O_2}$$

Most of the methods employed for the preparation of oxygen are instances of direct decomposition. The substance most frequently used is potassium chlorate, which is a compound of potassium, chlorine, and oxygen. At a comparatively low temperature the oxygen is driven off from this body, a compound of potassium and chlorine remaining behind.

$$\underset{\text{potassium chlorate}}{2KClO_3} = \underset{\text{potassium chloride}}{2KCl} + \underset{\text{oxygen}}{3O_2}$$

EXPERIMENT 8.—Using the same apparatus as that employed in the last experiment (Fig. 6), and placing in the test tube about enough potassium chlorate to fill the bottom of the tube half an inch, we apply heat gently to it. At first the salt crackles; this is owing to the

crystals being split up by the heat, and is known as ***decrepitation.*** The chlorate soon melts, and then appears to boil; the salt is really decomposed, owing to the disengagement of oxygen, as is easily proved by applying the spark test.

If, instead of using potassium chlorate alone, a mixture of that salt with about one-quarter of its weight of manganese dioxide (black oxide of manganese) is employed, the gas is evolved much more rapidly, more uniformly, and at a much lower temperature. The mode in which this oxide acts is at present obscure; it is, however, probable that it is converted into an unstable, higher oxide, continually formed and decomposed during the reaction. At the end of the experiment the manganese dioxide is always found unaltered.

This method of preparing oxygen is the one usually employed in laboratories, except when the oxygen is required in a state of absolute purity.

The student will require seven jars of oxygen to perform the following experiments. It will be found to be the most convenient way to prepare two jars of the gas at a time.

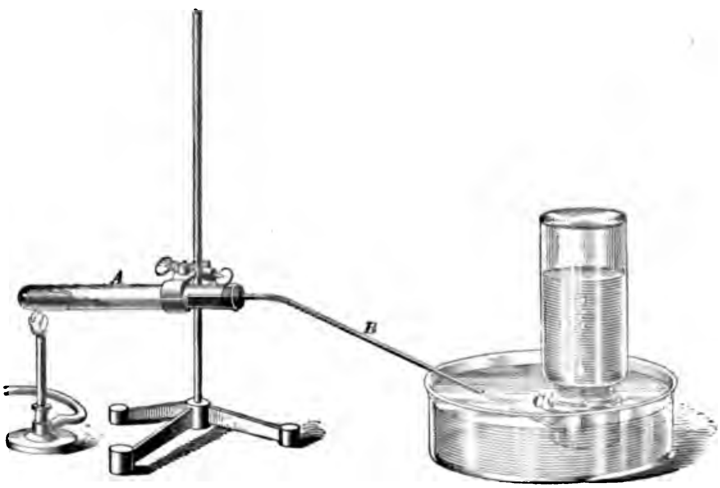


FIG. 7.

**EXPERIMENT 9.**—Fill a 6-inch test tube about one-third with the mixture of potassium chlorate and manganese dioxide in the proportion mentioned before: this amount is sufficient to evolve the quantity of

oxygen required. Push a wire down to the bottom of the tube, so as to make a free passage for the gas. Connect the test tube *A*, Fig. 7, to a delivery tube by means of an air-tight fitting cork, and run this delivery tube *B* into the pneumatic trough to the side opening of the beehive shelf *C*; have three collecting jars filled to the brim with water in readiness. Holding the Bunsen burner in the hand, commence warming up the mixture gently at the top, i. e., at the end nearest the cork, and slowly bring the flame nearer the bottom as the gas is evolved. The reason for this is that the mixture cakes on being heated; if heated first at the bottom, the upward current of gas would carry the loose dust of the mixture on with it, and probably choke the delivery tube. Withdraw the Bunsen burner when the third jar is about half full. Remove then the end of the delivery tube from the trough; otherwise, as the hot gas within cools, the contraction will draw up the water and crack the test tube.

EXPERIMENT 10.—To one jar filled with oxygen add some water in which you have previously dissolved some lime (one-half of a test tube full of water is quite sufficient); see that the solution of lime is clear; shake the lime water and the oxygen up well, and observe that the lime water remains as clear as it was originally. Apply the spark test to the same jar after shaking up.

EXPERIMENT 11.—To the second jar filled with oxygen add a solution of litmus and shake up; notice that the blue color of the litmus solution remains unchanged.

EXPERIMENT 12.—In the third jar burn a piece of charcoal. Take your deflagrating spoon, fit over it a piece of cardboard or tin (the latter preferable), so that the spoon will reach to about one-third of the height of the jar from the bottom. Put the charcoal on the spoon and ignite it with the Bunsen burner; when glowing, plunge the spoon into the jar of oxygen till the cardboard covers the mouth of the jar; it burns brightly. When the combustion is over, remove the deflagrating spoon, pour in some lime water and shake up; notice that the lime water becomes *milky*.

If you shake a jar of oxygen with any kind of liquid, always cover the jar with a piece of plate glass; also, when you lift the jar from the pneumatic trough.

For the remaining experiments two more jars may be filled in the ordinary way over the pneumatic trough; another jar must be wiped perfectly dry and filled by *downward displacement;* i. e., do not use the pneumatic trough, but place the jar in which you intend to collect the oxygen mouth upwards; lead the delivery tube to the bottom of the jar, and

evolve the oxygen as has been already described. Oxygen, being somewhat heavier than air, will slowly drive the air out of the jar. Apply a glowing taper or match to the mouth of the jar, which will be at once relighted when the vessel is full of oxygen.

For the next experiment use a deflagrating jar; that is, a jar open at the top and bottom—in fact, simply a strong glass cylinder. Cork up the upper opening and fill the cylinder over the pneumatic trough with oxygen; allow it to stand in the pneumatic trough, after it is filled, till you use it.

EXPERIMENT 13.—Take a piece of watch spring; make it into a spiral and weigh it carefully. Next fasten it to a piece of cardboard, and attach to the other end of the wire a small piece of wood (a short piece of a match serves well). The watch spring is now ready for burning. The deflagrating jar, mentioned before, is then removed from the pneumatic trough into a flat porcelain dish, in the bottom of which a piece of writing paper has been placed and allowed to become saturated with the water in the dish. There will thus be a layer of about half an inch of water at the bottom, then the paper, and underneath that another thin layer of water. Loosen the cork at the top, light the piece of wood attached to the steel spring, and drop the spring as quickly as possible into the jar, closing it with the piece of cardboard fixed to the end of the spring (see Fig. 8). You will notice that it burns brilliantly, throwing out a number of sparks, while from time to time drops of molten oxide fall to the bottom; these are so hot that if allowed to come in contact with the porcelain dish they would fuse into the glaze even after falling through an inch or so of cold water. The stiff writing paper momentarily arrests their fall and thus gives them time to cool. When the burning is over, remove the unburnt end of the spiral; collect very carefully the whole of the globules of oxide of iron, place them in a crucible, and thoroughly dry them with a gentle heat. Weigh the

FIG. 8.

oxide and the remainder of the iron; notice that there will be a sensible increase of weight over that of the iron alone previous to the burning. The increase is due to the oxygen present in the iron oxide.

EXPERIMENT 14.—In another jar of oxygen, collected over the pneumatic trough, immerse, with help of the deflagrating spoon, a piece of sulphur, previously lighted over the Bunsen burner; notice the brilliant light with which the sulphur burns in the oxygen. Add to the jar, after the burning, some litmus solution; notice that this originally blue liquid is turned red.

EXPERIMENT 15.—In the other jar filled with oxygen burn a piece of phosphorus about the size of a small pea. It is one of the most brilliant experiments with oxygen. A very neat apparatus for this purpose is shown in Fig. 9. A light wire tripod has a ring at its upper part for supporting a globe which contains the gas, and just below it a shallow cup containing water, into which the neck of the globe enters. From the center of this cup rises a piece of wire, crowned with a small cup to serve as a receptacle for the phosphorus. The globe is filled about four-fifths with oxygen and then inverted on the stand. When all is ready, a piece of phosphorus is *very thoroughly dried* between two pieces of blotting or filter paper. The globe being raised, the piece of phosphorus is dropped into the receptacle, inflamed by touching it with a hot wire, and the globe replaced. The combustion is at once exceedingly vivid, but after a few seconds the phosphorus becomes volatilized by the heat, and begins to burn throughout the entire volume of oxygen with a brilliancy almost inconceivable.

FIG. 9.

EXPERIMENT 16.—In the jar of oxygen, which has been obtained by downward displacement, a piece of metallic sodium is to be burned. Sodium possesses such an affinity for oxygen that it has to be kept in some liquid which does not contain that element. Naphtha is usually employed for that purpose. Cut off a little piece about the size of a small pea, being *very* careful that the knife and everything that touches the metal is *perfectly dry*. Place in a clean and *dry* deflagrating spoon, heat in the Bunsen burner until it just glows, then put it in the jar of gas; it burns brightly; the products of combustion, which are solid, remain in the spoon. Allow it to get quite cool, then place the spoon in a little water in a beaker and dissolve off the oxide of sodium. To some litmus solution in a test tube add just a drop of dilute sulphuric acid. Pour the red solution thus obtained into the

**beaker containing the oxide of sodium; the blue color of the litmus will be immediately restored.**

On a large scale, oxygen is manufactured by a process devised by Brin. Air is forced into specially prepared porous barium oxide $BaO$ at a temperature below redness, and barium dioxide $BaO_2$ is formed. The stream of air is cut off and the barium dioxide is heated to redness, the pressure in the apparatus being lowered by air pumps at the same time. The oxygen absorbed is now disengaged, and the barium dioxide is converted into monoxide ready to absorb more oxygen.*

To make quantities of oxygen suitable for filling the gas holders of the laboratories of colleges and universities, the mixture (mentioned in Experiment 9) of potassium chlorate and manganese dioxide is heated in a sheet-iron or copper retort (Fig. 10). At a bright redness manganese dioxide

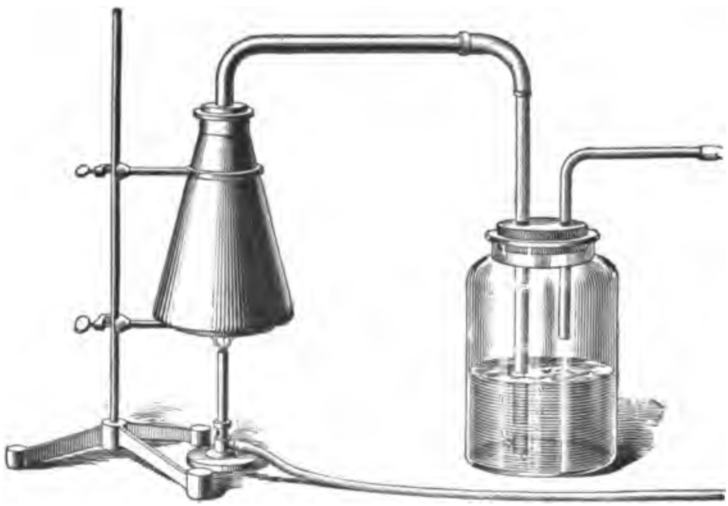

FIG. 10.

gives up one-third of its oxygen and is converted into red oxide of manganese.

* Oxygen is now sold in New York, and other large cities, in strong steel bottles, from which it may be conveniently drawn as required for experiments.

$$\underset{\text{manganese dioxide}}{3MnO_2} = \underset{\text{red oxide of manganese}}{Mn_3O_4} + \underset{\text{oxygen}}{O_2}$$

Powdered potassium dichromate may also be heated with twice its weight of concentrated sulphuric acid, oxygen being disengaged.

$$\underset{\text{potassium bichromate}}{2K_2Cr_2O_7} + \underset{\text{sulphuric acid}}{8H_2SO_4} = \underset{\text{potassium chromium sulphate}}{4KCr(SO_4)_2} + \underset{\text{water}}{8H_2O} + \underset{\text{oxygen}}{3O_2}$$

**11. Properties.**—Oxygen is an odorless, colorless, and tasteless gas, somewhat heavier than air, its specific gravity being 1.1056. It is slightly soluble in water, 100 volumes of water at 15° C. dissolving about 3 volumes of oxygen. Oxygen is strongly magnetic; calling the magnetism of iron 1,000,000, that of oxygen is 377; hence, the magnetic power of atmospheric oxygen is quite appreciable. The diurnal variations of the magnetic needle are due, at least partially, to variations in the intensity of this magnetism, owing to the changes of temperature. Among its properties, by far the most important is that it possesses the power of supporting respiration. Oxygen in the pure state, however, is too active, so that a diluting agent is required; in the atmosphere this is supplied by the presence of nitrogen in large quantities. It also supports the combustion of inflammable bodies, though not itself inflammable. All substances that burn in the air burn with increased vigor and brilliancy in oxygen. Oxygen, owing to its chemical activity, is capable of entering into combination with all elements except fluorine; but, in the state in which it is usually obtained, heat is necessary to accomplish this union. The class of bodies thus formed is an important one, to which the name of *oxides* has been given (see Art. **46,** *Theoretical Chemistry*). The preceding experiments show the formation of several of these. The composition of the bodies produced is expressed in the following equations:

$$\underset{\text{carbon (charcoal)}}{C_2} + \underset{\text{oxygen}}{2O_2} = \underset{\text{carbon dioxide}}{2CO_2}$$

| | | | | | | |
|---|---|---|---|---|---|---|
| $S_2$ | + | $2O_2$ | = | $2SO_2$ |
| sulphur | | oxygen | | sulphur dioxide |
| $P_4$ | + | $5O_2$ | = | $2P_2O_5$ |
| phosphorus | | oxygen | | phosphorus pentoxide |
| $2Na_2$ | + | $O_2$ | = | $2Na_2O$ |
| sodium | | oxygen | | sodium oxide |

There is one important point of distinction between various oxides that the student may have observed in performing the last experiments: one group, of which sulphur dioxide is a representative, reddens a solution of litmus; another series, represented by sodium oxide, is characterized by the property of restoring the blue color to a litmus solution that has been previously reddened by an acid.

The oxides of the first group, when dissolved in water, produce *acids;* those of the second group are known as *bases*.

**12. Uses.**—Oxygen is used in the arts for increasing the intensity of combustion, for purposes of either light or heat.

Various methods have been proposed for its manufacture from the atmosphere. The most efficient of these are:

1. **Tessie du Motay's,** which consists, first, in passing pure air over a heated mixture of manganese dioxide and sodium hydrate, producing, by its oxygen, sodium manganate; and, second, in heating this manganate still higher, by which, with the aid of a current of steam, it is decomposed into the original materials again, setting the oxygen free.

2. **Deville's,** which consists in the decomposition of sulphuric acid by heat.

3. **Brin's,** which has been previously described.

In the natural world the uses of oxygen are nearly infinite. Diluted with nitrogen in the air, it is continually entering into and issuing from chemical combinations, setting free in the former, and absorbing in the latter, enormous stores of energy. It is by the respiration of oxygen that the energy of living beings is set free from their food; it is, again, by the separation of oxygen by the sunlight that energy is stored

up anew in the food. It has been calculated that 6,000,000,000 pounds of oxygen are daily consumed in the respiration of living beings, and that the daily consumption of oxygen, for all purposes, reaches the incredible sum of 7,142,857 tons. There is, however, little cause to fear an exhaustion of the supply, since the air of the globe, even if no oxygen were daily added, is supposed to contain sufficient of this gas to supply the enormous demand for, approximately, 480,000 years.

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## OZONE.

*Allotropic oxygen. Formula* $O_3$. *Molecular weight 47.88. Density 23.94. One liter weighs 2.145 grams (23.94 criths).*

**13. History.**—The repeated discharges of an electric machine develop a peculiar odor, which is due to the production of a body discovered by von Marum in 1785. It was not, however, until 1840 that any searching investigations were made upon this subject. Then Schönbein noticed the similarity between this electrical odor and that produced in the electrolysis of water, and showed that, in both cases, the substance produced turned paper, moistened with a solution of potassium iodide and starch, to a deep blue color. In the same year Marignac and De la Rive proved this substance to be a modification of oxygen. In 1852 Becquerel and Fremy discovered a process by which pure oxygen could be entirely converted into *ozone*. In 1860 Andrews and Tait showed that a contraction of volume occurred when oxygen became ozone, which means that 3 atoms of oxygen, in forming 1 molecule of ozone, occupy the same volume as 1 molecule of oxygen composed of 2 atoms; and, in the same year, Soret showed that oil of turpentine possessed the property to absorb the entire molecule of ozone. In the same year Andrews proved that the substance in the air which affected test paper in the manner above described was *ozone*.

**14. Preparation.**—Ozone is produced by the passage of a series of electric sparks through either air or oxygen,

and may, as has been already told, be recognized by its peculiar odor whenever an electric machine is worked. The quantity of ozone thus obtained is, however, very small, but if a *silent electric discharge* is passed through the gas, care being taken to avoid sparks, a much larger portion of oxygen will undergo this transformation. In order to effect this, arrangements are made so that the discharge occurs between large surfaces placed very near each other.

EXPERIMENT 17.—To perform this experiment a special apparatus is required. It consists of a thin, white glass tubing *a b*, as shown in (*a*), Fig. 11, which is closed at the bottom, except that a long piece of small-

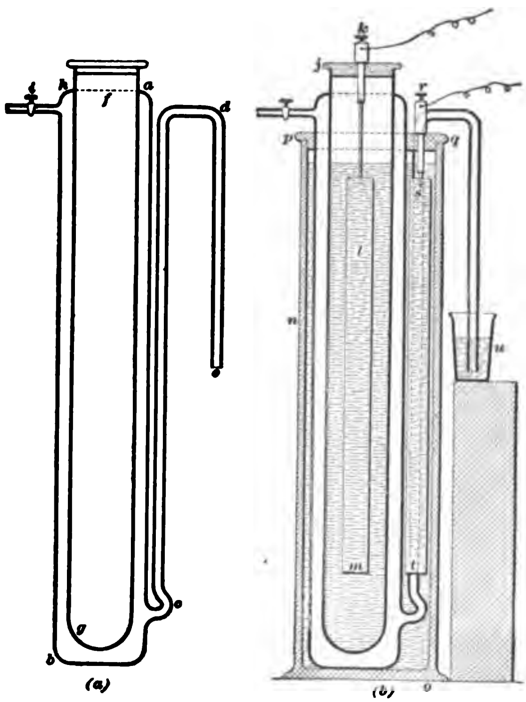


FIG. 11.

bore glass tubing *c d e* is sealed into it at *c*, this tube being bent over in the shape shown in the figure. Inside the tube *a b* is fixed another one of smaller size *f g*, open at the top, but closed at the bottom similar to a test tube. These tubes are sealed to each other by fusion of the glass

at *h*; immediately below this joint a side quill glass tube carrying a stop-cock *i* is fused into the outer tube. Between the tubes *a b* and *fg* there is, consequently, an annular space. If air is admitted at *i*, it traverses this space, and afterwards makes its exit through the tube *c d e*. This constitutes the ozone-producing apparatus proper; in (*b*) it is shown fixed in an outer jar, and provided with other fittings, in order to provide means for passing an electric current from the surface of *a b* to that of *fg* across the intervening annular space and through any gas contained in this space. The ozone tube proper is simply drawn separately in (*a*), in order that its construction may be more readily understood.

Turning to (*b*), the tube *fg* is fitted with a cover *j*, to which is attached a binding screw *k*, and a platinum wire and a sheet platinum foil *l m* (electrode). The whole tube *a b* and inner limb *c d* of the small tube are contained within the outer glass jar *n o*, and are held in their place by the cover *p q*. Through this cover passes the binding screw *r*, carrying also a platinum electrode *s t*. To use the apparatus, fill the outer jar *n o* nearly to the top with dilute sulphuric acid (1 to 10), and also fill the inner tube *f g* to the same level with the same liquid. To the binding screws *k*, *r*, attach copper wires leading from the terminal of a powerful induction coil. In turning on the electric current, it is conducted by means of the electrodes to the dilute sulphuric acid, which again conducts it to the surfaces of the tubes *a b* and *fg* arranged within each other; it then passes across the ring-like space as a silent discharge.

Having the apparatus so far in readiness, support a small beaker *u* containing water so as to receive the end *e* of the exit tube. Open the stop-cock *i*, and pass dry oxygen into the apparatus until it has displaced the air from the annular space between the tubes. (For this purpose, a volume of oxygen, about four or five times that of the annular space, should be passed through the tube.) Next close the stop-cock *i*, and observe that the tube *de* is full of gas. Turn on the electric current from the induction coil through the apparatus; ozone is gradually formed, and the water rises in the tube *d e*, showing that the volume of the gas within is diminishing.

Having noted the diminution of volume, remove the beaker *u* and replace it by a small gas jar arranged for collection by *downward displacement*. Pass a slow current of oxygen through the stop-cock *i*, and collect the emergent gas in the gas jar. Under most favorable circumstances, however, the quantity of ozone produced by the transformation of oxygen does not amount to more than about one-sixth of the outflowing gas.

**15. Properties.**—Physically, ozone closely resembles oxygen, except in density, which is just 1.5 times that of

oxygen. Chemically, it also resembles oxygen, as all its compounds are oxides. In fact, it is oxygen with properties intensified, and may be termed *active oxygen.* It possesses a peculiar odor, sometimes described as resembling that of weak chlorine. Hautefeuille and Chappuis have liquefied it by allowing the strongly compressed gas to expand suddenly; the liquid thus obtained is sky blue and the compressed gas has the same color, the blue tint becoming more intense as the temperature is lowered or the pressure increased. At a temperature of 290° it is reconverted into ordinary oxygen.

Its most remarkable property is its energetic oxidizing power. Many of the metals, including even those so difficult to oxidize as copper, mercury, and silver, are rapidly converted into oxides by ozone.

During oxidation by ozone no diminution of the volume of the gas occurs. In oxidation by ozone, it is, in fact, the extra volume of oxygen that enters into combination, the normal oxygen set free occupying the same space as the original ozone. This fact is represented in the following equation:

$$\underset{\text{ozone}}{O_3} + \underset{\text{silver}}{2Ag} = \underset{\substack{\text{silver}\\\text{oxide}}}{Ag_2O} + \underset{\text{oxygen}}{O_2}$$

Ozone bleaches strongly, and is poisonous to animal life on account of its irritating effects upon the mucous surfaces. It is soluble in oil of turpentine only. The oxidizing power of ozone leads it to immediately decompose potassium iodide when the two are brought into contact, oxidizing the potassium and setting the iodine free.

$$\underset{\text{ozone}}{O_3} + \underset{\substack{\text{potassium}\\\text{iodide}}}{2KI} + \underset{\text{water}}{H_2O} = \underset{\substack{\text{potassium}\\\text{hydrate}}}{2KHO} + \underset{\text{iodine}}{I_2} + \underset{\text{oxygen}}{O_2}$$

**16. Tests.—Schönbein's test** is based on this property of ozone. It consists of paper moistened with a dilute solution of potassium iodide and starch. The iodine is set free by the ozone and colors the starch deep blue.

**Fremy's test** is paper moistened with an alcoholic tincture of guaiacum; it is turned to a light-blue color by ozone.

Paper moistened with manganous sulphate or lead hydrate becomes dark brown or black in ozone.

EXPERIMENT 18.—To prepare Schönbein's test paper, put a piece of starch, the size of a large shot, into a test tube, and add some water; shake up thoroughly and boil over the Bunsen burner; add a piece of potassium iodide, of about the same size as the starch, and allow it to dissolve. Dip some pieces of filter paper in the solution, and introduce one of these pieces into a jar filled with ozone. A blue tint is immediately produced on the paper.

**17. Occurrence.**—Ozone occurs free in the atmosphere surrounding us, and its odor is frequently noticeable after thunderstorms with violent electric discharges. It is also produced by the decay of animal and vegetable matter and probably by the growth of plants. One of its chief functions in nature is to oxidize, and thus destroy, impurities in the air. It is asserted that 1 volume of air, containing $\frac{1}{6000}$ part of ozone, will purify 540 volumes of putrid air. Atmospheric ozone burns up miasmatic exhalations, and in this way preserves a natural state of purity in the air.

**18. Uses.**—Ozone has found utility in the arts as a bleaching agent and as a disinfectant.

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## SUMMARY.

**19.** Oxygen occurs plentifully in nature and is widely distributed. It was discovered in 1774 by Priestley. It may be prepared by the decomposition of mercuric oxide, potassium chlorate, or manganese dioxide. Remember that manganese dioxide assists the decomposition of potassium chlorate without itself undergoing any noticeable change. Oxygen forms compounds called *oxides*, one group of which reddens litmus paper. Another class restores the blue color to the litmus paper thus reddened. It is a colorless, odorless, and tasteless gas, supporting respiration and combustion, but is not inflammable by itself. It is neutral to litmus in its action by itself.

Ozone is a condensed form of oxygen, possessing a peculiar

odor, sometimes likened to that of chlorine. It is produced by the passage of electricity through air. It is much more active than oxygen.

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### OBJECT DEMONSTRATION.

**20.** Observe the appearance and general characteristics of the following: potassium chlorate, a colorless salt occurring in tabular or flat crystals; manganese dioxide, a heavy, black powder, produced by grinding the natural form of the substance; iron oxide, which is produced by the combustion of iron in oxygen, and consists of brittle molten globules.

Study carefully the apparatus and general arrangements for the production of ozone (Experiment 17 and Fig. 11).

Starch is a white powder, which dissolves, on heating, to a pasty liquid. Potassium iodide is a white, deliquescent salt, occurring in cubic crystals.

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### LABORATORY DIRECTIONS.

**21.** In Arts. **10, 14,** and **16,** a number of very important and instructive experiments have been described. Experiments 13, 15, and 17 are generally confined to the lecture table, and the performance of the others must be left to the discretion of the student. Note, however, in each case the general arrangement of the apparatus, and the general lesson each experiment is intended to convey. Experiments 7, 9, 14, and 16 should, however, if possible, be performed by the student.

For the generating apparatus (Fig. 7), take a test tube $\frac{5}{8}$ of an inch in diameter and 5 inches long. Select a cork that just fits it, and soften the cork by rolling it under your foot. Take a piece of glass tubing, about 18 inches long, and bend it to the shape shown in Fig. 12, and round off the edges. (Directions for bending glass tubing and rounding the sharp edges are especially given in Arts.

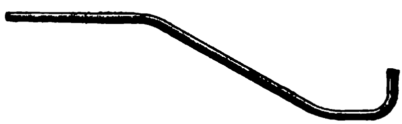

FIG. 12.

**125-127,** *Theoretical Chemistry.*) Next, it will be necessary to bore a hole in the cork. For this purpose an instrument called a *cork borer* is furnished; it consists of a set of several thin, brass tubes, the lower ends of which are sharpened. A rod is also contained in the set, in order to thrust out of the borer the pieces of cork cut from the holes. The rod can also be pushed through two holes in the top of the borer, forming a handle to grasp when boring. Before beginning to bore, see that the borer is clear; then, starting at the *small* end of the cork, bore carefully by twisting the borer and pushing it through. Take care, while going on, that the hole is perfectly *straight*. Do not place the cork against a table or bench and bore into the wood, as this would blunt the borer and diminish its usefulness. The hole should be *cut*, *not bruised*, through. The borer selected should be just a trifle less in diameter than the glass tubing you are going to use. This will insure an air-tight fitting. It will be found of advantage to rub a little grease on the glass tube, in order to facilitate its passage through the hole of the cork. While attempting to force the glass tube into this hole, protect your hand with a duster, in case it should break. Remember that the success of your experiments depends, to a large degree, on the fact that the cork, as well as the glass tube, fits perfectly *air-tight*. Much time and trouble is saved by fixing up every piece of apparatus as *nearly perfect as possible*.

In the special sketches, subsequently given, the student may often adapt bent glass tubes, already made, by the use of rubber connections, instead of making new ones of the exact shape shown.

The terms *leading tube* and *delivery tube* are applied to the tube by which a gas emerges from any particular piece of apparatus.

For experiments, gases are usually collected in *gas jars*. Any wide-mouthed pickle jar or milk bottle will answer this purpose; they should, however, be made of white glass.

The gas is most easily retained in any bottle by placing a ground-glass plate on the mouth, which should be ground

flat. This is very quickly and easily done thus: Take a piece of ordinary plate glass; place on it some emery of medium coarseness, and moisten it with water; then take the bottle, hold it firmly, mouth downwards, on the plate, and rub in a circular motion. A minute's rubbing will generally be quite sufficient to grind the top true. The joint between the glass plate and the bottle is rendered air-tight by smearing the glass plate with a little grease. (*Resin cerate*, obtainable in every druggist's store, may be recommended for this purpose.)

**22.** Gases that are only slightly soluble or entirely insoluble in water are, as a rule, collected over the pneumatic trough filled with water. Gases that are soluble in water are collected either over the pneumatic trough filled with mercury, or, more conveniently, by the process of *displacement*.

In this operation the gas pours into the bottle and drives the air out. If the gas is heavier than the air, stand the bottle upright, and let the delivery tube from the generating apparatus reach to the bottom of the bottle. After the bottle is filled, cover it with a piece of glass or cardboard, in order to prevent the escape of the gas by diffusion. In order to find out if the bottle is entirely filled with the gas, test from time to time near its mouth. The test employed, of course, depends entirely on the nature of the gas; oxygen, as has been already stated, for instance, may be recognized by its property of igniting a glowing spark.

Should the gas be lighter than the air, the whole arrangement must then be inverted; the gas is then said to be collected by *upward displacement*.

## COMPOUNDS OF OXYGEN WITH HYDROGEN.

### HYDROGEN OXIDE, OR WATER.

*Formula* $H_2O$. *Molecular weight 17.96. Density 8.98. One liter of water vapor weighs .8064 gram (8.98 criths). Specific gravity 1. Solidifies at 0°. Boils at 100°.*

**23. History.**—Until 1776 water was considered an element, when Lavoisier proved its compound nature. Cavendish and Watt, in 1781, proved its composition by synthesis, and in 1805 Humboldt and Gay-Lussac ascertained the ratio of its constituents to be 1 : 2, while Berzelius and Dulong succeeded in proving its combining ratio by weight to be 1 : 8.

**24. Occurrence.**—Water, either free or combined, occurs most abundantly in nature. Natural waters are, however, rarely pure, owing to their great solvent power, and even rain water is more or less contaminated, carrying very seldom less than 3 per cent. of foreign substances, principally constituents of the atmosphere, with it. It is well known that water is an essential to animal and vegetable life. Seven-eighths of the entire human body is water.

**25. Preparation.**—Water occurs so plentifully in nature that, except when required for chemical purposes, no special process of preparation is necessary. Chemically pure water is obtained by freeing the natural water from the foreign substances it usually contains, and, as most of these are solids in a state of solution, the water is purified by the *process of distillation* (see Art. **101,** *Theoretical Chemistry*).

**26. Properties.**—Between the temperatures of 0° and 100°, water is a colorless, tasteless, and limpid liquid. When seen in large masses it shows a distinct, greenish-blue tint. It is neither acid nor alkaline in its action on vegetable colors; it is a poor conductor of heat and a non-conductor of electricity. Its most important property is its solvent power; there exist comparatively few substances that it does not dissolve in larger or smaller quantities. The oceans are the natural reservoirs from which our water supplies are drawn. By the heat of the sun, immense quantities of sea-water are converted into vapor, which either remains suspended in the air, or condenses to produce clouds. Special atmospheric conditions lead to the precipitation of this moisture as rain

or snow. Rain and snow are the direct or indirect sources of spring and river water; these latter always contain more or less solid matter, depending on the condition of rock and soil over or through which they have been passing. The rivers always carry down with them a certain proportion of solid matter to the ocean, which is left when the water is again vaporized to form clouds. In this way occurs a continuous, though slow, increase in the quantity of matter found in sea-water, which, as a result, has its well known saline taste. The constitution of sea-water naturally varies to a certain extent, according to locality and climate, but its principal constituents always are sodium chloride, magnesium, and a number of other salts, of which iodine and bromine are the most important participants.

EXPERIMENT 19.—Evaporate to dryness on a clean piece of platinum foil a few drops of water, notice that a perceptible residue remains; repeat the same experiment with a few drops of distilled water, and compare the results.

**27. Natural Waters.**—Water is never met in an entirely pure state in nature, as has been previously stated. Whether it has rested upon, or has flowed over, the surface of the soil; whether it has fallen in the form of dew, mist, or rain; or whether it has just emerged from its subterranean passages, it always contains more or less solid matter in a state of solution.

The purest form of natural water is rain water. Other natural waters may be divided into *potable*, or *drinkable*, *mineral*, and *saline waters*.

*River* and *lake waters*, especially such as are found in granite regions, are, as a rule, the purest. The water of Loch Katrine, in Scotland, for instance, does not contain more than 2 grains of solid matter to the gallon, and is one of the purest natural waters known. The purest water supplied to any city in the United States is that from Lake Cochituate, which furnishes the city of Boston with its water supply, and which, according to the reports of the Boston City Board of Health, contains only 3.11 grains of impurities to

the gallon; the Schuylkill water, which supplies Philadelphia, contains 3.50 grains; the waters collected in the reservoirs of Ridgewood, for the supply of Brooklyn, 3.92 grains, the Croton water of New York City, 4.78; Lake Michigan, from which Chicago draws its water supply, 6.68 grains in every gallon. The water of the Thames, which, to a great extent, supplies London, contains nearly 16.68 grains of impurities to each gallon.

*Spring* and *well water*, owing to the fact that they have, previous to their issue, penetrated the soil, are never as pure as surface waters. Thus, the water of a well near Central Park, New York City, gave 43.54 grains; one in Schenectady, 49.21 grains; one in Amsterdam, Holland, 69.93 grains, and one in London, England, 99.97 grains of solid matter to the gallon.

*Mineral* and *saline waters* are those that, by virtue of their chemical constituents or temperature, have a certain effect on the animal economy, and hence possess a therapeutic (medicinal) value.

They are either *cold* or *warm;* they are termed warm when they possess, at the moment of their issue, a temperature above 15°. Their thermal state, of course, varies, covering the whole range of the thermometer from 15° to 100°. There are numerous hot springs in Virginia, Colorado, and California. The temperature of the "Grand Geyser," in Iceland, is far above 100°.

According to their chemical constituents, mineral waters are classified in a number of characteristic groups, distinguished either by the predomination of certain constituents, or by the presence of certain distinctly active components. These waters may be distinguished as follows:

*Acidulous*, or *gaseous*, *waters*, characterized by the presence of free carbonic-acid gas.

*Alkaline waters*, characterized by the presence of a larger or smaller proportion of sodium bicarbonate, or of an alkaline silicate.

*Chalybeate waters*, characterized by holding an iron salt in solution.

*Saline waters*, i. e., those that contain neutral salts.

*Sulphur waters*, characterized by the presence of hydrogen sulphide and other soluble sulphides.

*Acidulous*, or *gaseous*, *waters* are distinguished by the presence of free carbonic acid, which is dissolved in the depth of the earth and under a pressure much greater than that of the atmosphere; hence, a certain portion of this gas becomes naturally disengaged as soon as the water emerges from the soil, thus creating more or less effervescence. Gaseous waters are cool, and their taste is pleasant at the moment of issue, but sometimes these waters become saline, or even alkaline, after the disengagement of the greater proportion of their carbonic-acid gas. Natural gaseous waters never consist of a solution of carbonic-acid gas in pure water; they always contain a certain quantity of saline matters, such as sodic, calcic, and magnesic carbonates, and sometimes even traces of chlorides and sulphates. Such is approximately the composition of certain of the *Saratoga springs*, and the well known *Seltzer water*.

*Alkaline waters*, as their name indicates, possess an alkaline reaction. This alkaline reaction is sometimes noticed immediately upon their emergence, sometimes only after the loss of their free carbonic acid. This reaction may be due to an alkaline silicate, but can generally be referred to an alkaline carbonate. Hydrosodium carbonate, $HNaCO_3$, popularly known as *bicarbonate of soda*, is present in nearly all waters of this class. *Vichy water*, for instance, contains nearly 5 grams of this salt per liter.

*Chalybeate waters* are distinguished by holding more or less iron in solution, which gives to these waters an astringent taste and certain therapeutic properties. The traces of iron they contain may exist in three conditions:

1. As ferrous carbonate held in solution by carbonic acid.

2. As ferrous crenate. Berzelius gave the name of crenic acid to a body which is related to peculiar acids existing in the soil, and which are known as ulmic, humic, and geic acids. Ferrous crenate is soluble in water; its constitution, however, is at present unknown.

3. As ferrous sulphate.

Hence, chalybeate waters may be carbonated, crenated, or sulphated.

Such waters, however, seldom contain ferrous salts in really considerable proportions; in fact, many ferruginous waters (i. e., waters containing ferrous salts) of undoubted sanative power do not contain more than about 4 centigrams of these salts per liter. Through exposure to air they lose the greater portion of their carbonic acid very soon, and ferrous carbonate is precipitated, which, in turn, soon loses its carbonic acid and is thus converted into brown ferric hydrate.

Springs of chalybeate water are numerous in this country as well as in Europe. They exist in Bedford, Pa.; Manitou, Colo.; Saratoga, N. Y., and many other places. The springs of Spa and Pyrmont, in Belgium; Bussang, in the Vosges; and Passy, near Paris, are known all the world over.

*Saline water* includes a great number of waters of varying composition, charged with neutral salts, among which the most prominent are the chlorides, bromides, and iodides. According to the predominating or most active constituent, they are classified as chlorinated, sulphated, and bromo-iodated waters.

Sea-water is a chlorinated water. It is a well known fact that it contains a notable proportion of sodium chloride. This common salt is accompanied by the chlorides of potassium and magnesium and by a considerable amount of magnesium sulphate.

*Sulphur water* contains a soluble sulphide or hydrogen sulphide. This class of waters is divided into two distinct classes; namely, *natural sulphur waters* and *accidental sulphur waters*. The first class contains sodium sulphide, is generally hot when emerging from the soil, and contains little solid matter. The second class of waters embraces those that are formed on the spot by the reduction of sulphates, and particularly calcium sulphate, contained in the waters. This reduction is accomplished by the action of organic matters which impregnate the soil, and of which the

combustible elements, carbon and hydrogen, remove the oxygen of the sulphates.

**28. Effects of Heat on Water.**—Among other properties of water, the physical changes it undergoes as a direct result of the application of heat are of such vast importance as to justify a somewhat extended description. It is a well known fact that, at a temperature below the freezing point, water exists in the solid state. Every one is familiar with ice. Taking a piece of ice at a temperature considerably below that at which it was formed, say $-20°$, the following is a description of its changes as a result of the continuous application of heat:

As heat is first applied, the ice rises in temperature, and at the same time increases in volume (expands); these changes proceed regularly until a temperature of 0° is attained. At that point the temperature remains stationary, notwithstanding the fact that the absorption of heat continues. During this time the ice melts, and the heat thus absorbed, without causing any corresponding elevation of temperature, is employed in converting the solid ice into liquid water. The heat necessary to melt a given quantity of ice at 0° into water at the same temperature would raise the same weight of water from 0° to 79°, a fact expressed in other words by saying that the *latent heat of water is 79 heat units.* During the melting of ice, a considerable diminution of volume occurs, only 10 volumes of water being produced by 10.9 volumes of ice. As soon as the whole of the ice is melted, the temperature once more begins to rise, and does so steadily, until a temperature of 100° is attained. From 0° to 4° the water diminishes in volume with an increase in temperature; at 4°, however, it begins to expand, and continues to do so until 100° is reached. At 4°, therefore, water is at its maximum density; either a diminution or an increase of temperature will result in expansion. At 100° the water begins to boil and remains stationary in temperature, but is not all at once converted into vapor; on the contrary, between five and six times as long is necessary to boil away

the whole of the water as was needed to raise it from the freezing to the boiling point. Or, to express it in exact figures, the quantity of heat necessary to convert a given weight of water into steam is sufficient to raise 537.2 times the same weight of water from 0° to 1°. The steam produced is at the same temperature, 100°, as the boiling water; this large amount of heat is employed in the conversion of the water from the liquid to the gaseous state. The whole of the water having been converted into steam, a further application of heat results in the expansion of the steam, which follows the general laws governing the relation of gases to heat.

In cooling, steam passes through a series of changes that are just the converse to those it experiences on being heated. During the condensation of steam into water, and the solidification of water to form ice, heat is liberated in the same quantity as was required in the first place to effect, respectively, the liquefaction of ice and the conversion of water into steam.

**29.** Chemically, water is an intensely active compound, entering into combination directly with most oxides, forming bases or acids, as the case may be, with the evolution of more or less heat. One of the most familiar examples of this is the slaking of lime, a process that may be represented by the following equation:

$$\underset{\text{calcium oxide}}{CaO} + \underset{\text{water}}{H_2O} = \underset{\text{calcium hydrate}}{Ca''(OH)_2}$$

Water also enters molecularly into the composition of many crystalline substances (see "Crystallography," *Theoretical Chemistry*), the amount appearing to increase in proportion as the crystallization takes place in a colder and more dilute solution. Calcium sulphate crystallized takes two molecules, $CaSO_4, 2aq$; copper sulphate, five, $CuSO_4, 5aq$; sodium sulphate, ten, $Na_2SO_4, 10aq$; etc. If such crystals are exposed to dry air, they *effloresce*, which means that they lose their water of crystallization and fall into an opaque, white powder.

Other crystallized substances, again, in a moist atmosphere, attract water and liquefy, which is termed *deliquescence*. It has already been mentioned that the solvent power of water is greater than that of any other liquid known; but, of course, each substance soluble in water has a certain limit of solubility, this limit depending on such conditions as temperature, pressure, etc.

Gases, as a whole, are much less soluble in hot than in cold water.

**30. Composition of Water by Volume.**—It has been previously stated that, until within the last hundred years, water had been considered as an element.

Experiments 1, 2, and 5 will have shown the student that the composition of water is compound, since, on the one hand, hydrogen has been obtained from it, and, on the other, water has been produced by the combustion of hydrogen in the atmospheric air.

By the application of intense heat, water may be separated into oxygen and hydrogen, but the difficulty met is that, as the gases cool down, they once more combine and reproduce water.

The most convenient source of the necessary heat to separate water into its constituents is the electric spark.

EXPERIMENT 20.—The necessary requirements to perform this experiment, which is mostly confined to the lecturer's table, consist of a piece of apparatus composed of a glass bulb *A*, Fig. 13, through which platinum wires *B*, *B* are so fixed that their ends are in the center of the bulb, and, approximately, an eighth of an inch apart. The lower part of this bulb *A* is provided with a glass tube, which passes through a cork fitted into the mouth of a bottle *C*. There is further fitted to bulb *A*, through a cork, a leading tube *D* passing into a pneumatic trough for the collection of any evolved gases. After the flask *C* is filled about one-half with water and the approaches reconnected, the water in *C* is boiled until the rising steam has expelled the whole of the air from the apparatus, the steam itself being condensed by the cold water in the trough. At this stage a series of sparks from an induction coil is passed through the wires *B*, *B*, and a small gas jar *E* is arranged to collect any gas escaping from *D*. The passage of each spark decomposes a small quantity of steam, and, the mixed gases being

immediately largely diluted with steam, some proportion, at least, is kept apart until the gases have cooled below their combining temperature. In this way the gas jar is slowly filled with an explosive

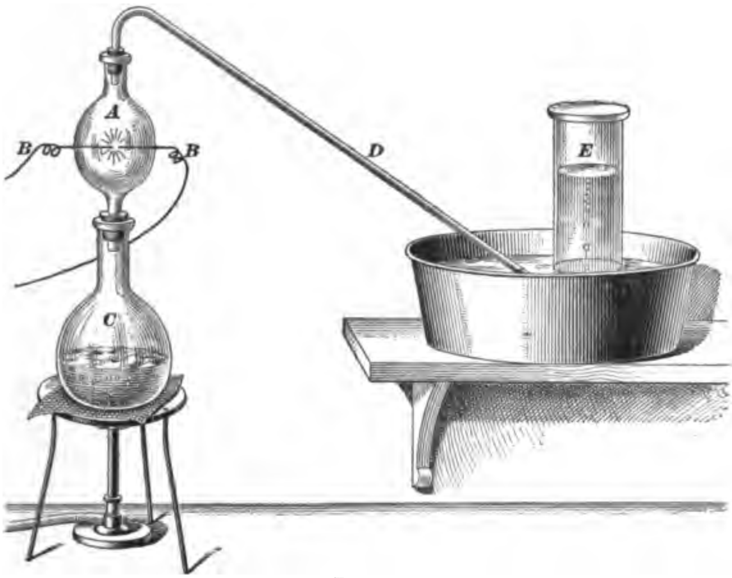


FIG. 13.

mixture of hydrogen and oxygen, the jar is removed, a light applied, and a violent explosion ensues.

**31.** The most convenient force to apply, for the purpose of the decomposition described above, is undoubtedly that of voltaic electricity. The following experiments on the analysis of water by electricity (electrolysis), and its synthesis, should, as the average student will not be able to perform them himself, be read very carefully; the directions given, and the general arrangement of the apparatus, as well as the results obtained, should be studied very carefully.

EXPERIMENT 21.—The electrolytic apparatus shown in Fig. 14 is to be attached by means of the wires to a battery consisting of two or three Bunsen's cells. Such an apparatus is easily constructed by taking a wide-mouthed bottle *A*, Fig. 14, of about 8 ounces capacity, and fitting it with a good cork, through which passes the delivery tube *B* and the necessary appliances for conveying a current of electricity to

the contained liquid. For this purpose a very convenient arrangement consists of the glass tubes *C*, *C*, as shown in the figure. Into the lower ends of these are fused pieces of platinum wire, to which small pieces


FIG. 14.

of platinum foil *D* are attached. These tubes are then to be filled with mercury, and the connection with the battery is readily made by pushing the clean ends of the wires into the liquid metal.

In order to use the apparatus, the bottle is filled to the neck with water, to which between 25 and 30 drops of sulphuric acid have been previously added. Then the battery is connected, and we soon notice that a stream of bubbles of gas ascends from each piece of platinum. The gas issuing from the leading tube is collected in a bottle over the pneumatic trough. When entirely full, the mouth is closed with a cork, carefully wrapped up in a duster, and after the cork is again removed and a light applied, a violent explosion of the gas will take place.

Further information may be gained from a modified form of this experiment, in which the gas evolved from each of the electrodes is separately collected.

EXPERIMENT 22.—A typical form of apparatus for this purpose is shown in Fig. 15, which consists of a shallow glass basin *A*, containing water to which a little sulphuric acid has been added (acidulated water), and two electrodes connected to the binding screws *B*, *B*. The glass tubes *C*, *C* are also filled with acidulated water, and each is inverted over one of the electrodes. Then the battery wires are connected to

the binding screws *B*, *B*, to which the electrodes have been attached. As soon as this connection has been made, it will be noticed that gas immediately begins to rise in each of the tubes, and it will soon be further noticed that in the tube inverted over the ***negative electrode***

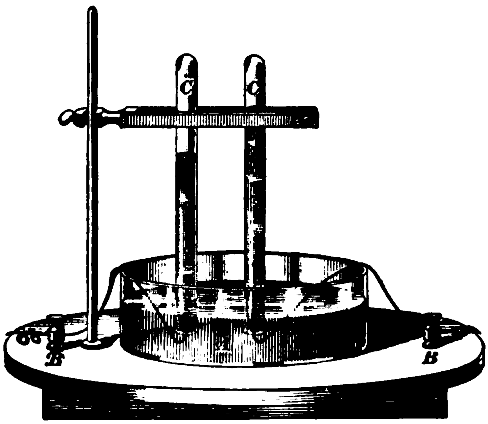

FIG. 15.

the volume is *double* that evolved from the *positive electrode*. When the tube containing the larger quantity of gas, i. e., the one over the negative electrode, is nearly full, it is removed, and a light applied to its mouth; the collected gas burns quietly, with the familiar blue flame of hydrogen. In the second tube of gas a glowing match is plunged, with the effect that it is instantaneously relighted, thus proving this gas to be oxygen.

These experiments, and especially the last one, No. 22, prove that water may be decomposed into its components, viz., hydrogen and oxygen, and, furthermore, that these components exist in water in the proportion of 2 to 1. One circumstance about this last experiment may be somewhat puzzling to the student, namely, that pure hydrogen is evolved at the one electrode, and pure oxygen at the other, while there is no sign of any transference of gas from the one to the other electrode through the liquid.

What becomes of the oxygen that was in combination with the hydrogen evolved at the negative pole, and what becomes of the hydrogen that was combined with the oxygen evolved at the positive pole?

We are able to explain this seemingly puzzling question by referring the student to the diagrammatic representation of water by electrolysis, as shown in Fig. 16.

In this diagram, $N$ and $P$ represent portions of the negative and positive electrodes, respectively, of the apparatus shown in Fig. 15. The series of circles by which these two poles are connected are supposed to represent a chain of

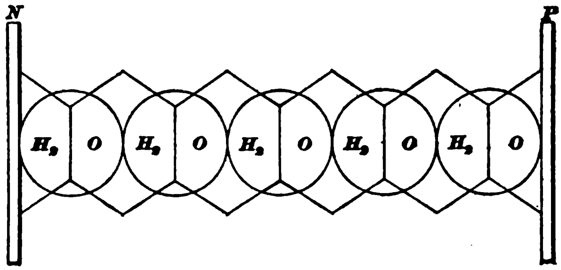


FIG. 16.

molecules of water, making complete contact between the two electrodes, which is indicated by each containing the formula of water $H_2O$. On the passage of an electric current, the molecule lying next to the negative electrode $N$ is decomposed, and its hydrogen liberated in the gaseous state. Its oxygen combines with the hydrogen of the next molecule to form water, and its hydrogen, in turn, decomposes the next adjoining molecule, until finally the molecule contiguous to the positive electrode $P$ is reached; the oxygen there, finding no other molecule to decompose, is liberated, and consequently escapes in the gaseous form. The formation of this second series of molecules is indicated in the diagram by the series of hexagons shown. If the electrode $P$ is formed of any easily oxidizable metal, such as zinc, the nascent oxygen combines with it to form an oxide, none escaping in the gaseous state.

**32.** The student should also learn that the reunion of oxygen and hydrogen again produces water.

EXPERIMENT 23.—The gas jar used for the collection of the mixed gases in the electrolysis of water, described in Experiment 21 and

shown in Fig. 14, is filled with water, which is then poured out into a graduated measuring tube; one-third of its contents is poured back into the gas jar, and the height of the water in it is marked by a file scratch on the outside of the bottle; another third is added and again marked in a similar way. This bottle so marked is then placed in the pneumatic trough filled with water, and from a jar, previously filled with oxygen, one-third of the original jar is filled with oxygen; this is

FIG. 17.

done in the manner shown in Fig. 17. After that, the remaining two-thirds of the bottle are filled in the same way with hydrogen. After removing the bottle from the pneumatic trough, it is shaken up, so as to cause a thorough diffusion of the two gases, the bottle is securely wrapped in a duster, in order to prevent injuries to the hands in case the bottle breaks, and a burning match applied to the mouth of the bottle. It explodes in just the same manner as the detonating gas collected by electrolysis.

The recombination of hydrogen and oxygen may also be effected with the aid of the electric spark, which is passed through a mixture of these gases. Cavendish made use, in his investigations, of a strong glass vessel, with two platinum wires inserted in it, so that the electric spark might pass through the gases between their ends. A form of this kind of apparatus is shown in Fig. 18. *A* represents the glass vessel, which, after being exhausted by an air pump, is attached to a graduated glass jar *B* containing a

mixture of 2 volumes of hydrogen and 1 volume of oxygen. On opening the stop-cock *C* the vessel fills with the mixture of gases. The stop-cock is again closed, and an electric spark is flashed through this mixture; drops of water will be noticed to condense on the sides of the vessel. This operation may be repeated a number of times, until the whole of the gases have been caused to combine; by this time there will be an appreciable quantity of water in the glass vessel.

FIG. 18.

**33.** For the purpose of measuring exactly the proportions in which hydrogen and oxygen unite, an instrument called a **eudiometer** is employed.

Fig. 19 represents a form of this apparatus, proposed by Ure; it consists simply of a **U**-shaped tube of glass closed at one end. The closed limb is graduated, and two platinum wires are fused near its extremity. This limb is to be filled with water, and then a given quantity of pure oxygen—20 cubic centimeters, for instance—is to be introduced from a delivery tube; 50 cubic centimeters of pure hydrogen are then similarly introduced, all measurements being made when the level of the liquid is the same in both limbs. The open end is closed firmly by the thumb, as represented in the drawing, a cushion, so to speak, of air

being left between it and the liquid, and an electric spark is passed through the mixture of hydrogen and oxygen by means of the platinum wires.

Upon restoring the level of the liquid by adding water, 10 cubic centimeters of gas will be left, which, on examination, will be found to be pure hydrogen.

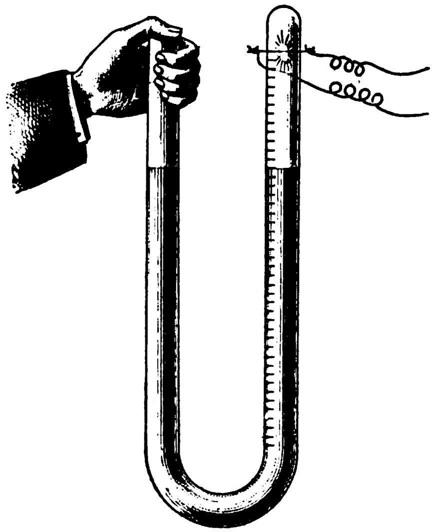

FIG. 19.

Hence, 20 volumes of oxygen have united with 40 volumes of hydrogen to form water, which is the ratio 1 : 2, which theory requires and which is expressed by the formula $H_2O$.

**34. Composition of Water by Weight.** The preceding experiments have shown the student the composition of water by volume, and it is necessary that he should also become acquainted with the means employed for the determination of the exact composition by weight. The synthesis by weight cannot be effected with accuracy by weighing the gases themselves, on account of their large volume. It is, therefore, accomplished by passing an indefinite quantity of hydrogen over a known weight of pure, hot oxide of copper, when hydrogen combines with the oxygen of the oxide to form water, according to the equation:

$$\underset{\text{oxide of copper}}{CuO} + \underset{\text{hydrogen}}{H_2} = \underset{\text{water}}{H_2O} + \underset{\text{copper}}{Cu}$$

The loss of weight suffered by the oxide of copper gives the amount of oxygen; and, if this is deducted from the weight of the water, the weight of hydrogen will be ascertained.

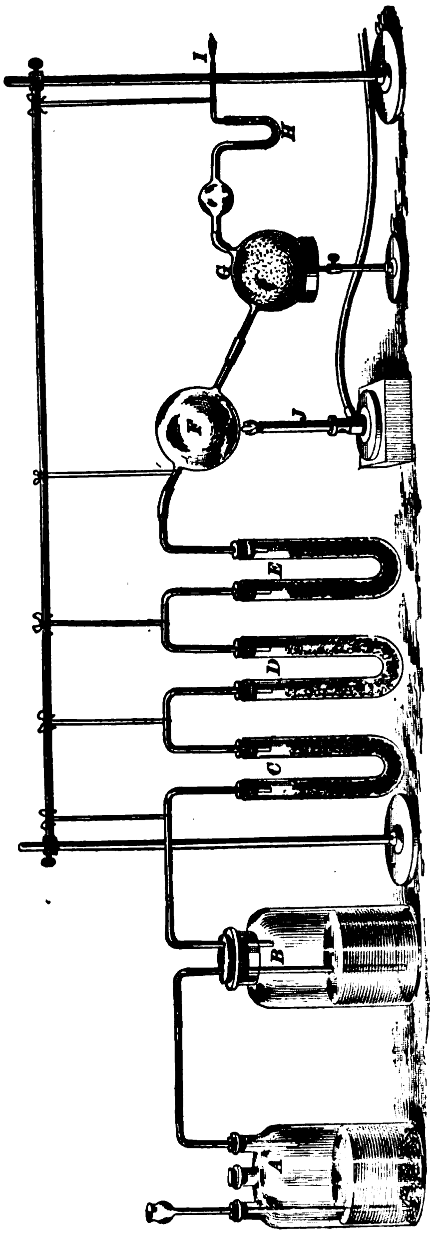


Fig. 20.

The apparatus employed for this purpose is represented in Fig. 20.

Experiment 24. — The apparatus shown in Fig. 20 consists of a generating bottle *A*, in which hydrogen is evolved by the action of zinc and sulphuric acid. To this is attached a wash bottle *B*, partly filled with a solution of caustic potash, in order to retain any traces of sulphuric acid that may be carried over mechanically by the evolved hydrogen. To this wash bottle are attached, by means of leading tubes and corks, three U-shaped tubes *C*, *D*, and *E*. The tube *C* contains pumice moistened with a solution of mercuric chloride; the tube *D* contains fragments of fused potash, and the tube *E* contains pumice moistened with strong sulphuric acid. The object of the wash bottle and these three tubes is to remove all impurities from the evolved hydrogen, thus allowing only perfectly *pure* and *dry* hydrogen to pass in to the bulb *F*. This bulb, or globe *F*, consists of a blown piece of combustion tubing, which is attached to *E* by a piece of rubber tubing, and is in such a position that a Bunsen burner may be placed underneath it. The

bulb *G*, also connected with *F* by a short piece of rubber tubing, is used for the collection of water, and is in turn connected with a drying tube *H*, filled with small pieces of calcium chloride.

Having this apparatus so far in readiness, about half an ounce of perfectly dry copper oxide is placed in the bulb *F*, and both are accurately weighed together. Then *G* and *H* are weighed separately and the apparatus reconnected, taking at the same time considerable care to make all joints perfectly air-tight.

By the addition of a small quantity of sulphuric acid to the generating bottle *A* through the funnel tube, in order to cause a slow evolution of hydrogen, the hydrogen passing through the entire outfit expels the air from it; as soon as pure hydrogen emerges from the jet *I*, the oxide of copper in the bulb *F* is slowly heated by means of the Bunsen burner *J*. It will soon be noticed that water is produced and that it collects in receiver *G* any traces of vapor being retained by the calcium chloride in *H*. After about ten minutes the burner *J* is removed, and the bulb *F* allowed to cool. As soon as this bulb has thoroughly cooled, the apparatus is disconnected; the generating bottle *A* is first removed, and air drawn through the tubes by blowing into the glass tubing leading into the wash bottle *B*; this is done in order to displace all hydrogen. Then the copper oxide globe *F* is disconnected and carefully weighed; the loss in weight represents the oxygen that has combined with hydrogen to form water. The bulb *G* and drying tube *H* are again weighed; their combined increase in weight is the water that has been produced.

Supposing, as the result of an actual experiment, that the oxide of copper has lost 16 decigrams of oxygen, the receiver and drying tube will be found to have gained 18 decigrams in weight. We would know therefore that water contains (very nearly) 16 parts by weight of oxygen and two parts by weight of hydrogen in 18 parts of it, or 8 parts by weight of oxygen to 1 part by weight of hydrogen.

**35. Oxyhydrogen Blowpipe.**—The energy with which hydrogen and oxygen combine has been utilized for the purpose of producing the highest temperature (3,000°) obtainable by any chemical process.

The *oxyhydrogen blowpipe*, as shown in Fig. 21, is an apparatus for burning a jet of hydrogen mixed with half its volume of oxygen. The gases are supplied from separate gas holders (usually bags with pressure boards and weights) through the tubes *A* and *B*, which conduct the two gases

to the brass sphere *C*. Each of these tubes is provided with a valve of oiled silk, opening outwards, so as to prevent the passage of either gas into the receptacle containing the other. The tube *D* is stuffed with fragments of very thin copper wire, which would rapidly conduct away the heat and extinguish the flame of the mixed gases burning at the


FIG. 21.

jet, should it tend to pass back and ignite the mixture in *C*. The stop-cocks *E* and *F* allow the flow of the gases to be regulated so that they may mix in the right proportions. If the hydrogen is kindled first, it will be found that, as soon as the oxygen is turned on, the flame is reduced to a very much smaller volume, because the undiluted oxygen required to maintain it occupies only one-fifth of the volume of the atmospheric air, from which the hydrogen was at first supplied with the necessary oxygen. The heat developed by the combustion being, therefore, distributed over a much smaller area, the temperature at any given point of the flame must be much higher, and very few substances are able to endure it without fusion.

*Lime* is one of these few substances; and, if a cylinder of

lime is supported, as at $G$, in the focus of the flame, its particles become heated to incandescence, and a light is obtained that is visible at night from very great distances, so as to be well adapted for signaling, lighthouses, etc.

If a shallow cavity is scooped in a lump of quicklime, a few small fragments of platinum placed in it and exposed to the oxyhydrogen flame (Fig. 22), a fused globule of platinum

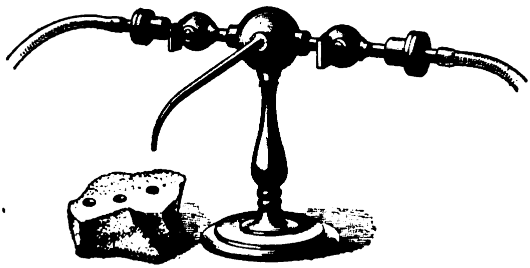

FIG. 22.

of considerable size may be obtained in a few seconds. Pipe clay, which resists the action of all ordinary furnace heat, may be fused into glass in this flame, while gold and silver are instantaneously melted and vaporized into a dense smoke.

**36. Tests of Water.**—As, according to the best medical authorities, cholera, diarrhea, and typhoid fever are propagated by certain *spores*, or *germs*, which are present in the evacuations of persons suffering from such maladies, and are conveyed into water that is allowed to become contaminated by sewage, a great deal of attention is directed, in the analysis of water intended for drinking and domestic purposes, towards the detection of organic matters containing nitrogen (so called *albuminoid matters*) which would be conveyed into the water in sewage. The analytical operations necessary for this purpose require great care and skill, and the conclusions drawn from their results are by no means finally agreed on among scientific chemists. (Water analysis will be extensively treated on in *Quantitative Analysis.*)

There are, however, a number of certain simple tests that may very often determine whether it is worth while to perform a more elaborate analysis of the water:

1. Pour half a pint of the water to be tested into a wide-mouthed bottle or decanter; close it with the palm of your hand, or, better, with a glass stopper, and shake it violently up and down. If an offensive odor is then perceived, the water is probably contaminated by sewage gas, and possibly with other constituents from the same source.

2. Add to a little of the water a drop or two of dilute sulphuric acid, and enough potassium permanganate (Condy's red fluid) to tinge it to a faint rose color; cover the vessel with a saucer or glass plate. If the pink tinge is still visible after a quarter of an hour, the water may be considered wholesome.

3. Pour a little solution of silver nitrate (lunar caustic) into a carefully *cleaned glass* and see that it remains transparent; then pour in some of the water; should a strong milkiness appear that is not cleared up on adding a little diluted nitric acid, the water probably contains sodium chloride, which always exists in sewage water, but very seldom in wholesome water in any considerable quantity, unless near the seacoast.

**37.** One of the most important points to be taken into account in estimating the qualities of a water is its action on lead, since this metal is so frequently employed for storage tanks and transmission pipes of water; and cases frequently occur in which the health has been seriously injured by repeated small doses of compounds of lead taken in water that has been kept in a leaden cistern or has been standing in leaden pipes.

To detect lead in a water, fill a tumbler with it; place this on a white sheet of paper, add a drop or two of diluted nitric acid and some hydrogen sulphide; a dark-brown tinge will be seen on looking through the water from above if there is any lead compound present.

### HYDROGEN PEROXIDE.

*Free hydroxyl. Formula* $H_2O_2$. *Molecular weight 33.92. Specific gravity of liquid 1.452.*

**38. History.**—This remarkable compound was discovered by Thenard in 1818, who called it *oxygenated water.*

**39. Preparation.**—Hydrogen peroxide is prepared from barium dioxide by the action of hydrochloric or, preferably, carbonic acid. The reaction that occurs may be represented by the following equation:

$$\underset{\text{barium dioxide}}{BaO_2} + \underset{\text{carbonic acid}}{H_2CO_3} = \underset{\text{barium carbonate}}{BaCO_3} + \underset{\text{hydrogen peroxide}}{H_2O_2}$$

By adding the materials alternately, the water present soon becomes saturated; then, by evaporation over sulphuric acid, this water may be removed, thus leaving pure hydrogen peroxide.

To prepare pure hydrogen peroxide, some barium dioxide $BaO_2$ is dissolved in as little diluted nitric acid as possible. To this solution one of barium hydroxide [baryta water $Ba(OH)_2$] is added; the precipitate $BaO_2,8H_2O$ is washed by decantation, and gradually added to diluted sulphuric acid (1 part of acid to 6 parts of water, by weight), care being taken to leave the liquid very slightly acid:

$$BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4$$

If the $H_2SO_4$ were added to the $BaO_2,8H_2O$ instead as recommended, the $H_2O_2$ would be decomposed by the remaining $BaO_2$ as fast as it would be formed. The precipitate is allowed to settle, and the clear liquid evaporated in the exhausted receiver of an air pump, over a dish of oil of vitriol to absorb the water, which evaporates much more rapidly than the hydrogen peroxide.

**40. Properties.**—Pure hydrogen peroxide is a colorless, syrupy liquid, of specific gravity 1.452, and possesses a slight chlorous odor. It dissolves in ether, and is slightly volatile in steam. Its most remarkable feature is the facility with

which it is decomposed into water and oxygen. (The presence of a little free acid renders it rather more stable, while the presence of free alkali has the opposite effect. A solution of hydrogen peroxide, containing a little hydrochloric acid, is sold for medicinal and photographic purposes, for bleaching ivory, cleaning old pictures, hair dye, and various other uses.)

At about 21°, it begins to decompose and to evolve bubbles of oxygen. At 100° it decomposes with violence.

The mere contact with certain metals, such as gold, platinum, and silver, which have no direct attraction for oxygen, will cause the decomposition of the peroxide without any chemical alteration of the metal itself. (Such inexplicable changes are sometimes included under the general denomination of *catalysis*, which means "decomposition by contact.")

Manganese dioxide $MnO_2$ decomposes hydrogen peroxide without undergoing any change; but, if an acid is present, the $MnO_2$ will be reduced to $MnO$, and will pass into solution as a manganous salt. The most surprising effect is that which takes place with silver oxide. If a drop of hydrogen peroxide is allowed to come in contact with silver oxide, which is a brown powder, decomposition takes place with explosive violence and the evolution of great heat. The silver oxide loses its oxygen and becomes gray, metallic silver. The oxides of gold and platinum are attacked in a similar manner.

These extraordinary changes, which are, as has been already mentioned, usually described as *catalytic actions*, may be, however, accounted for on the hypothesis that the oxygen in the oxides of silver, gold, etc. exists in a condition different from that of the second atom of oxygen in hydrogen peroxide, and that these two conditions of oxygen have a chemical attraction for each other, which may be compared with that existing between certain different elements. If the oxygen in the silver oxide is represented as electronegative (see Table 7, *Theoretical Chemistry*), as its relation to this metal would lead us to expect, and the second atom of oxygen in hydrogen peroxide is represented as electropositive oxygen, the mutual decomposition of the two compounds may be represented according to the following equation:

$$Ag_2\bar{O} + H_2O\overset{+}{O} = Ag_2 + H_2O + \bar{O}\overset{+}{O}$$

Most elementary substances, with few exceptions, have molecules composed of two atoms, which may be due to the circumstance that each atom is the electric complement of the other.

If hydrogen peroxide, even in diluted solution, is added to potassium permanganate that has been previously acidified with a little sulphuric acid, its original red color is entirely destroyed, and bubbles of oxygen are evolved, causing effervescence. The chemical reaction occurring may be represented by the following equation:

$$\underset{\text{potassium permanganate}}{K_2Mn_2O_8} + \underset{\text{sulphuric acid}}{3H_2SO_4} + \underset{\text{hydrogen peroxide}}{5H_2O_2}$$

$$= \underset{\text{potassium sulphate}}{K_2SO_4} + \underset{\text{manganous sulphate}}{2MnSO_4} + \underset{\text{water}}{8H_2O} + \underset{\text{oxygen}}{5O_2}$$

A compound so ready to part with its oxygen as hydrogen peroxide will naturally act as a powerfully oxidizing agent. Thus it comes about that hydrogen peroxide acts not only as a reducing but also as an oxidizing agent. If some black lead sulphide is treated with hydrogen peroxide, it is rapidly oxidized to white lead sulphate, according to the equation:

$$\underset{\text{lead sulphide}}{PbS} + \underset{\text{hydrogen peroxide}}{4H_2O_2} = \underset{\text{lead sulphate}}{PbSO_4} + \underset{\text{water}}{4H_2O}$$

**41. Tests.**—A very striking reaction of hydrogen peroxide is that with chromic acid. If a solution of $H_2O_2$ is added to a weak solution of potassium bichromate acidified with sulphuric acid, the beautiful blue color of perchromic acid appears, a reaction which probably is expressed by the following equation:

$$\underset{\text{potassium bichromate}}{K_2Cr_2O_7} + \underset{\text{sulphuric acid}}{H_2SO_4} + \underset{\text{hydrogen peroxide}}{H_2O_2}$$

$$= \underset{\text{potassium sulphate}}{K_2SO_4} + \underset{\text{water}}{H_2O} + \underset{\text{perchromic acid}}{H_2Cr_2O_8}$$

After a little time, however, the blue color changes to a very pale green, the perchromic acid $H_2Cr_2O_8$ being decomposed by the sulphuric acid, yielding green chromium sulphate and free oxygen, which adheres in bubbles to the side of the vessel:

$$\underset{\text{perchromic acid}}{H_2Cr_2O_8} + \underset{\text{sulphuric acid}}{3H_2SO_4} = \underset{\text{chromium sulphate}}{Cr_2(SO_4)_3} + \underset{\text{water}}{4H_2O} + \underset{\text{oxygen}}{2O_2}$$

If the blue solution is shaken with a little ether, which dissolves the perchromic acid and rises with it to the surface, where it forms a blue layer, the color is much more lasting, and very minute quantities of hydrogen peroxide may thus be detected. Still more delicate tests for hydrogen peroxide are the production of a yellow color with *titanic acid* and a yellowish precipitate with *uranium salts.*

### SUMMARY.

**42.** Water is a widely distributed liquid, which, however, owing to its great solvent power, is never found pure in nature. Heat changes its condition from solid to liquid, and from liquid to gas. Water is decomposed by electricity into an explosive mixture of gases, each of which, however, may be separately collected; the gases recombine to again form water. By volume, water consists of 2 volumes of hydrogen and 1 volume of oxygen, which condense on union to form 2 volumes of steam. By weight, water contains 16 parts of oxygen to 2 parts of hydrogen.

Hydrogen peroxide, the second compound of oxygen and hydrogen, differs from water in that it contains an extra atom of oxygen in the molecule. This second atom is, however, held somewhat loosely; hence, this compound is readily decomposed into water and free oxygen. It acts as a reducing as well as an oxidizing agent.

## CHLORINE.

*Symbol Cl. Atomic weight 35.37. Valence I, III, V, and VII. Density 35.37. Specific gravity 2.435. Molecular weight $Cl_2$ 70.74. Melting point —102°. Boiling point —33.6°*

*at ordinary atmospheric pressure. 1 liter weighs 3.17 grams (35.37 criths) at 0°.*

**43. History.**—Chlorine was discovered by Scheele in 1774, who called it *dephlogisticated muriatic acid*, a name that was afterwards changed by Berthollet to *oxymuriatic acid*. It was first recognized as an element by Gay-Lussac and Thenard in 1809, and by Sir Humphry Davy in 1810, who gave it the name it now bears.

**44. Occurrence.**—This element is never found in the uncombined state, but is very abundant in the mineral world as sodium chloride, magnesium chloride, potassium chloride, and calcium chloride. Sodium chloride, or salt, exists in sea-water, mineral springs, and in the solid form in the earth, forming vast deposits, many of which are mined.

**45. Preparation.**—Chlorine may be prepared:

1. By the action of electricity or heat on chlorides:

$$\underset{\text{platinic chloride}}{PtCl_4} = \underset{\text{platinous chloride}}{PtCl_2} + \underset{\text{chlorine}}{Cl_2}$$

2. By the superior affinity of oxygen for hydrogen, as when, for instance, hydrogen chloride acts on manganese dioxide:

$$\underset{\substack{\text{hydrogen chloride}\\ \text{(hydrochloric acid)}}}{4HCl} + \underset{\text{manganese dioxide}}{MnO_2} = \underset{\text{manganous chloride}}{MnCl_2} + \underset{\text{water}}{2H_2O} + \underset{\text{chlorine}}{Cl_2}$$

3. By heating together sodium chloride (salt), sulphuric acid, and manganese dioxide:

$$\underset{\text{sodium chloride}}{2NaCl} + \underset{\text{sulphuric acid}}{2H_2SO_4} + \underset{\text{manganese dioxide}}{MnO_2}$$

$$= \underset{\text{manganese sulphate}}{MnSO_4} + \underset{\text{sodium sulphate}}{Na_2SO_4} + \underset{\text{water}}{2H_2O} + \underset{\text{chlorine}}{Cl_2}$$

EXPERIMENT 25.—The apparatus necessary for the preparation of chlorine is shown in Fig. 23. The materials employed are placed in a

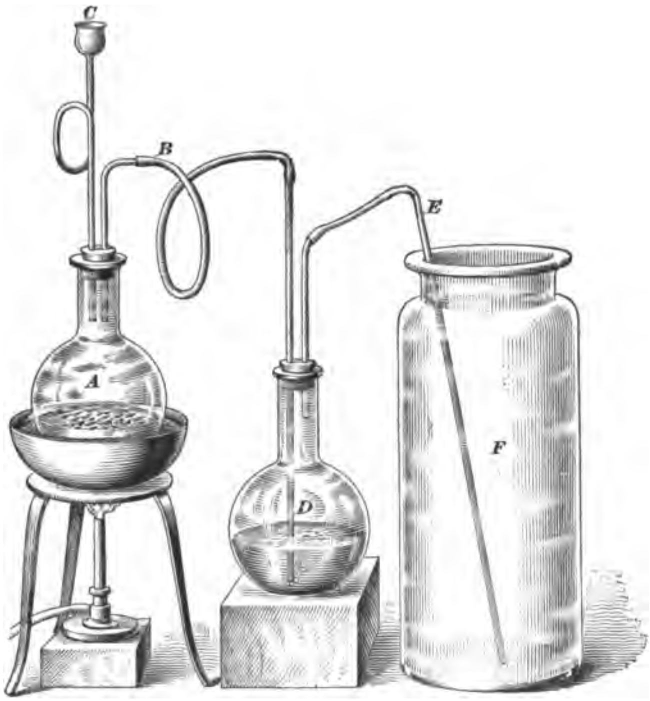


FIG. 23.

flask *A*, which stands in fine, dry sand contained in a shallow iron basin (known as a *sand bath*) upon an iron tripod, beneath which a Bunsen burner is placed. Through the cork of flask *A* two tubes pass, one *B* for the delivery of the gas, the other a safety tube *C*. This safety tube *C* is a funnel tube or thistle tube bent twice upon itself, as clearly shown in Fig. 23. The object of this safety tube is to prevent the escape of the evolved chlorine; that is, when any liquid is poured into the funnel, a small portion remains in the bend and acts as a valve, or seal, thus preventing the escape of the gas evolved in the flask. To the delivery tube *B* is attached, by means of a piece of rubber tubing, a bottle *D* containing sulphuric acid, to the bottom of which a glass tube passes, and through which the gas is made to bubble, in order to dry it. From this drying bottle it passes through a rubber-tube connection and a long piece of glass tubing *E* to the bottom of a collecting jar *F*, where, being heavier than air, the gas gradually collects. When full, a fact easily ascertained from the green color of the gas, the

mouth of the collecting bottle is closed with a glass plate smeared with a little tallow.

For every liter of chlorine gas, 8 grams of manganese dioxide and 20 grams of hydrochloric acid (5¼ cubic centimeters of manganese dioxide and 16 cubic centimeters of hydrochloric acid, according to the measuring glass furnished) are required. The acid is placed in the flask first, the manganese dioxide is then added, and the whole thoroughly shaken up. The evolution of chlorine goes on for a time without heat, but to complete the operation the Bunsen burner beneath must be lighted.

*Precaution.*—In experimenting with chlorine, great care should be taken to avoid the escape of this gas. Have every possible window open while evolving it, so as to allow as much access of fresh air as possible. Remember that the inhalation of chlorine will produce a serious inflammation of the respiratory organs.

In order to extract chlorine from common salt, the salt is heated with black oxide of manganese (manganese dioxide)

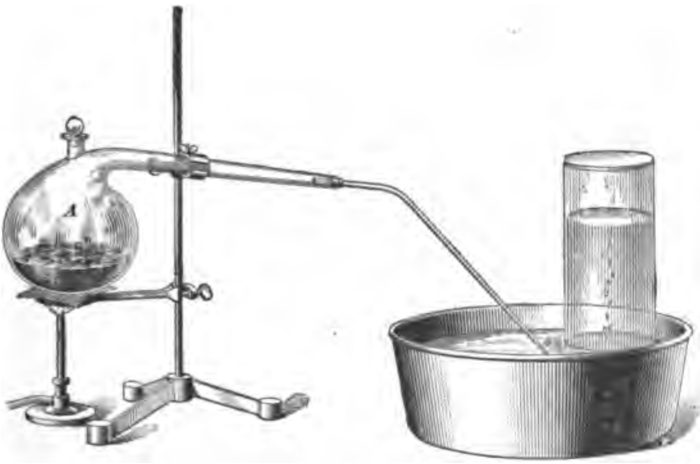


FIG. 24.

and diluted sulphuric acid, when the sulphates of sodium and manganese are left in solution and chlorine escapes in the gaseous form:

$$2NaCl + 2H_2SO_4 + MnO_2 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

EXPERIMENT 26.—Ten grams (or 9 cubic centimeters, according to the measuring cylinder) of common salt may be mixed with 7.5 grams

(or 5 cubic centimeters) of manganese dioxide, introduced into a retort *A* (see Fig. 24), and a cold mixture of 11 cubic centimeters of sulphuric acid with 27.5 cubic centimeters of water poured upon it. The retort having been well shaken to wet the powder thoroughly with the acid, a very gentle heat is applied, and the gas is collected in bottles filled with water and inverted in the pneumatic trough. When the bottles are filled, the corks, or stoppers, previously greased, must be inserted in them under water. The first bottle will contain the air from the retort, and will, therefore, have a paler color than the pure chlorine afterwards collected.

The measures given in Experiment 26 will fill about two 1-pint bottles.

*Precaution.*—The bottles of chlorine prepared as given in the last experiment should, owing to the chlorine being moist, be preserved in the dark, in order to avoid an explosion.

On a large scale, chlorine is manufactured by heating manganese dioxide with hydrochloric acid in stone stills.

In *Weldon's "manganese recovery process"* for the manufacture of chlorine, the manganese is made to act as a carrier of oxygen from the atmosphere to the hydrogen of the hydrochloric acid, setting the chlorine free.

For this purpose the manganous chloride, obtained according to the equation

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

is decomposed by lime:

$$\underset{\text{manganous chloride}}{MnCl_2} + \underset{\text{calcium oxide (lime)}}{CaO} = \underset{\text{calcium chloride}}{CaCl_2} + \underset{\text{manganous oxide}}{MnO}$$

By mixing the manganous oxide $MnO$ with more lime $CaO$ and blowing air through the mixture, manganese dioxide $MnO_2$ is reproduced, and may be again employed for decomposing a fresh quantity of hydrochloric acid.

**46. Properties.**—Chlorine is a yellowish-green gas, and possesses a peculiar suffocating odor and astringent taste. It is totally irrespirable, producing coughing if inhaled in a

very dilute state, and serious inflammation of the air passages if inhaled in larger quantities. It is two and one-half times as heavy as air (specific gravity 2.435), and may be reduced to the liquid state by cooling it to $-34°$, or by subjecting it to a pressure of 4 atmospheres at ordinary temperature; the chlorine thus reduced is a dark-yellow liquid of specific gravity 1.38. Chlorine gas is quite soluble in water, 1 volume of which at 11° dissolves about 3 volumes of the gas, forming a solution that possesses essentially the properties of the gas itself.

If a bottle of chlorine is held mouth downwards in water, its stopper removed, one-third of the chlorine decanted into a jar, and the rest of the gas shaken with the water in the bottle, the mouth of which is closed by the palm of the hand, as shown in Fig. 25, the water will quickly absorb about twice its volume of the gas, thus producing a partial vacuum in the bottle. If air is then permitted to enter and the bottle again shaken so long as any absorption takes place, a *saturated solution of chlorine* (*liquor chlori*, *chlorine water*) may be obtained.

FIG. 25.

By exposing this chlorine water to a temperature of about 0°, yellow crystals of *hydrate of chlorine* $Cl_4H_2O$ are obtained.

It should here be remarked that, when collecting chlorine gas over the pneumatic trough and the water therein happens to be very cold, the gas often has a foggy, opaque appearance in consequence of the deposition of minute crystals of hydrate of chlorine. On standing, the chlorine slowly becomes clear, crystals of the hydrate being deposited like hoarfrost upon the sides of the bottle; the gas also becomes clear when the bottle containing it is plunged into warm water.

The most characteristic chemical feature of chlorine is its wonderfully strong attraction for other substances, combining with all elements except oxygen, nitrogen, and carbon.

EXPERIMENT 27.—Put a small piece of phosphorus in the deflagrating spoon, and, without lighting it, place in a jar filled with chlorine. Notice that it commences to burn spontaneously, but does not evolve a very bright light.

EXPERIMENT 28.—Powder very finely some metallic antimony, and drop a little of it into a jar of the gas; it immediately takes fire. Into another bottle drop a small piece of thin copper foil; notice that it also immediately takes fire.

For the next two experiments, dry bottles are required; they must be, consequently, first wiped thoroughly dry with a duster, and then the chlorine collected in them as directed in Experiment 25.

EXPERIMENT 29.—Take a small piece of sodium in a *dry* and *clean* deflagrating spoon; heat in Bunsen flame until it is quite melted; plunge it in the dry jar of gas; it burns with the production of great heat, and white fumes of common salt are deposited.

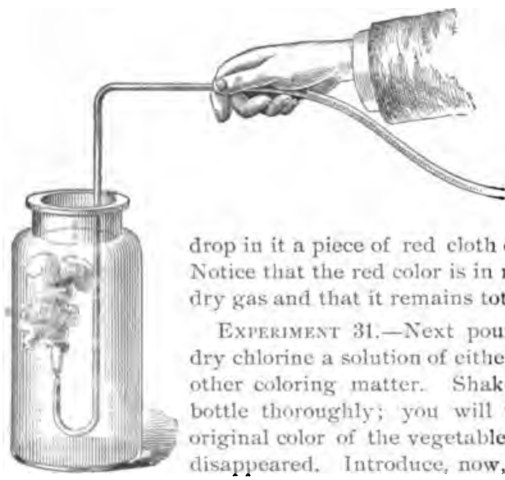

FIG. 26.

EXPERIMENT 30.—Take the other dry jar of chlorine and drop in it a piece of red cloth or red blotting paper. Notice that the red color is in no way affected by the dry gas and that it remains totally unchanged.

EXPERIMENT 31.—Next pour into the same jar of dry chlorine a solution of either litmus, indigo, or any other coloring matter. Shake the contents of the bottle thoroughly; you will then notice that the original color of the vegetable solution has entirely disappeared. Introduce, now, a piece of red cloth or red blotting paper, and you will see that this is also bleached.

We have learned here by actual experience that chlorine possesses the property of destroying vegetable colors, but that the presence of water is absolutely necessary for the operation of bleaching to take place.

EXPERIMENT 32.—Fit up, again, the apparatus used for the generation of hydrogen from zinc and sulphuric acid; attach to it a jet with a piece of rubber tubing, as shown in Fig. 26. Evolve the hydrogen in the

manner described in Experiment 4, and, after taking the usual precautions (see description of Experiment 5), light the jet and introduce it into a jar of chlorine; notice that the gas continues to burn, and that copious fumes are formed. At the same time the yellow tint, characteristic of chlorine, disappears.

The affinity of hydrogen and chlorine for each other is so great that many organic compounds containing hydrogen are entirely decomposed by chlorine.

EXPERIMENT 33.—Take a piece of tow, pull it as loose as possible, saturate with turpentine (a hydrocarbon with the formula $C_{10}H_{16}$); drop this into a jar filled with chlorine gas; it is decomposed with the evolution of light and heat. The carbon is deposited as soot; the hydrogen again produces fumes of hydrochloric acid.

The student will now have verified by his own observation many of the properties that chlorine possesses.

Like oxygen, chlorine is a supporter of combustion and is not inflammable; it is an extremely active element, forming bodies called chlorides. It possesses a most remarkable attraction for hydrogen; on exposing a mixture of those gases to diffused daylight, they slowly combine. Bright sunlight effects their immediate union with explosion. Carbon does not burn in chlorine, and, if bodies containing it are burned, the carbon is deposited in the free state. One important peculiarity of the combustion of bodies in chlorine is that they very often spontaneously ignite.

As a rule, although a lower temperature is sufficient for the commencement of the formation of chlorides, the heat evolved during the union is far less than that evolved in the production of the corresponding oxides.

The chemical actions occurring in Experiments 27, 28, 29, 32, and 33 may be represented by the following equations:

$$\underset{\text{phosphorus}}{P_4} + \underset{\text{chlorine}}{10Cl_2} = \underset{\text{phosphorus pentachloride}}{4PCl_5}$$

$$\underset{\text{antimony}}{Sb_2} + \underset{\text{chlorine}}{5Cl_2} = \underset{\text{antimony pentachloride}}{2SbCl_5}$$

$$\underset{\text{sodium}}{Na_2} + \underset{\text{chlorine}}{Cl_2} = \underset{\text{sodium chloride}}{2NaCl}$$

$$\underset{\text{hydrogen}}{H_2} + \underset{\text{chlorine}}{Cl_2} = \underset{\text{hydrochloric acid}}{2HCl}$$

$$\underset{\text{turpentine}}{C_{10}H_{16}} + \underset{\text{chlorine}}{8Cl_2} = \underset{\text{hydrochloric acid}}{16HCl} + \underset{\text{carbon}}{5C_2}$$

The attraction of chlorine for hydrogen enables it to effect the decomposition of water. If a solution of chlorine in water is exposed to the rays of the sun, bubbles are observed to rise to the surface, which, on examination, are found to be oxygen. At the same time, the solution loses its characteristic yellow color. The experiment is best performed by inverting a glass jar, filled with the solution, in a trough, also containing saturated chlorine water At a higher temperature, the decomposition takes place with much greater rapidity.

EXPERIMENT 34.—Connect a flask *A*, Fig. 27, fitted for the prepara-

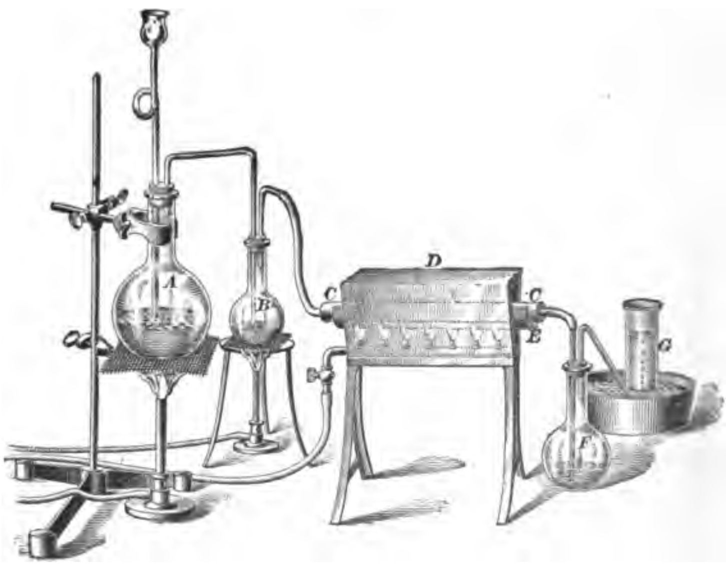


FIG. 27.

tion of chlorine, to the second flask *B*, which contains water, the leading tube from *A* dipping beneath the water level. Through the gas-tube

furnace $D$ pass a porcelain tube $CC$, filled with fragments of broken porcelain, and fitted at each end with corks and glass tubes. The danger of cracking the porcelain tube is lessened by placing it in a semicircular iron trough $E$, just large enough for the tube to lie in. The flask $F$ is a wash bottle, containing a solution of caustic potash, for the purpose of removing the hydrochloric acid and any excess of chlorine; the oxygen passes over, and is collected in the jar $G$. The tubes $B$ and $F$ are connected to the porcelain tube by pieces of rubber tubing. The furnace must first be lighted and the tube raised to redness; then light the Bunsen burners under both the chlorine and the water flasks; a mixture of chlorine and steam enters the furnace, decomposition ensues, and oxygen and hydrochloric acid escape.

**47.** The combination of hydrogen with chlorine may obviously be regarded as the substitution of an atom of chlorine for an atom of hydrogen in a molecule of hydrogen, $HH + ClCl = HCl + HCl$, the atom of hydrogen substituted having been removed as $HCl$. Viewed in this way, it becomes typical of a large number of cases in which 2 atoms of chlorine react with a hydrogen compound, one of them bearing away a hydrogen atom in the form of hydrogen chloride, while the other replaces the hydrogen thus removed. This substitution of an element, in this case chlorine, for hydrogen, is termed *metalepsis*, and is a reaction of chlorine with hydrocarbons that occurs very frequently; and, since the formation of hydrogen chloride is initiated by light, it is not surprising that metalepsis is aided by it. When equal volumes of marsh gas $CH_4$ and chlorine are mixed and exposed to sunlight, the volume of the mixture remains unaltered; but after a short time the yellow color of the chlorine disappears, and the gas is found to consist of equal volumes of methyl chloride and hydrogen chloride, $CH_4 + Cl_2 = CH_3Cl + HCl$. The metalepsis may be carried further by mixing methyl chloride with more chlorine, $CH_3Cl + Cl_2 = CH_2Cl_2 + HCl$; and, again, $CH_2Cl_2 + Cl_2$ will yield *chloroform* $CHCl_3$, and this with $Cl_2$ will yield carbon tetrachloride $CCl_4$. By mixing 1 volume of marsh gas with its own volume of $CO_2$, to prevent violent action, and adding 4 volumes of chlorine, an oily mixture containing $CHCl_3$ and $CCl_4$ is formed under the influence of daylight.

Since water is decomposed by chlorine, as we have seen from Experiment 34, it will not seem surprising that most other hydrogen compounds are attacked by it too. Ammonia $NH_3$, for instance, is acted on by chlorine with great violence. If a stream of ammonia gas, issuing from a tube connected with a bottle in which a solution of ammonia is heated, is passed into a bottle of chlorine, it takes fire immediately, burning with a peculiar flame, and yielding thick white clouds of ammonium chloride:

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$$

When chlorine is allowed to act on ammonium chloride $NH_4Cl$, its operation is less violent; but one of the most explosive substances, *nitrogen chloride* $NCl_3$, is produced.

Many of the compounds of hydrogen with carbon are also decomposed with violence by chlorine. When a piece of folded filter or blotting paper is saturated with turpentine $C_{10}H_{16}$, and afterwards plunged into a bottle containing chlorine, it suddenly bursts into a red flame, liberating thick clouds of carbon and hydrochloric acid. (This is only another form of Experiment 33. It is obvious that neither the tow nor the blotting paper is directly connected with the obtained results.) Acetylene $C_2H_2$ has been found to explode spontaneously with chlorine when exposed to light.

The attraction of chlorine for hydrogen enables the moist gas to act as an oxidizing agent. Thus, if marsh gas and chlorine are mixed in the presence of water, and exposed to the daylight, the water is decomposed, its hydrogen combining with the chlorine and its oxygen with the carbon of the marsh gas, according to equation:

$$\underset{\text{marsh gas}}{CH_4} + \underset{\text{water}}{2H_2O} + \underset{\text{chlorine}}{4Cl_2} = \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{hydrogen chloride}}{8HCl}$$

**48.** The powerful bleaching action on organic (vegetable) coloring matter shown in Experiment 31 is now easily understood. If a solution of chlorine in water is poured into a solution of indigo (sulphindigotic acid), for instance, the blue color of the indigo is discharged and gives place to a

pale-yellow tint. The presence of water is, as we have seen from Experiments 30 and 31, essential to the bleaching of vegetable colors by chlorine; the dry gas does not affect the color of dry vegetable dyes. The indigo is first oxidized at the expense of the water and converted into *isatin*, which is then acted on by the chlorine and converted by metalepsis into *chlorisatin*, having a brownish-yellow color:

$$(1)\quad \underset{\text{indigo}}{C_{16}H_{10}N_2O_2} + \underset{\text{water}}{2H_2O} + \underset{\text{chlorine}}{2Cl_2} = \underset{\text{isatin}}{2C_8H_5NO_2} + \underset{\text{hydrogen chloride}}{4HCl}$$

$$(2)\quad \underset{\text{isatin}}{C_8H_5NO_2} + \underset{\text{chlorine}}{Cl_2} = \underset{\text{chlorisatin}}{C_8H_4ClNO_2} + \underset{\text{hydrogen chloride}}{HCl}$$

Nearly all organic (vegetable as well as animal) coloring matters contain carbon, hydrogen, nitrogen, and oxygen, and are converted by moist chlorine into products of oxidation or chlorination that are, as a rule, either entirely or nearly colorless.

Chlorine is largely employed for bleaching linen and cotton, the gas acting on the coloring matter without injuring or affecting the fiber of these materials; silk or wool, however, presents considerably less resistance to chemical action, and would be, consequently, more or less injured by chlorine; hence, for bleaching these materials, sulphur dioxide is mostly preferable.

The irritating effects of chlorine on the human organism, however, offer a serious obstacle to the employment of chlorine or its solution in water on a large scale, so that it is usually used for these purposes in the form of *chloride of lime*, from which it can be easily liberated as it is wanted.

**49.** The explanation given above concerning the bleaching effect of chlorine may be applied, also, to its so called disinfecting power. The atmosphere, in certain localities, is occasionally contaminated with micro-organisms, some of which are only known through their injurious effects on the health, as they do not appear in the analysis of air, owing to their minuteness. Since, however, this minute

form of life appears to be killed by the same substances that are usually found to decompose organic compounds, chlorine has been very commonly and successfully employed to fight those invisible enemies of our health.

Among the dangerous and offensive products of putrefaction of animal and vegetable matter, hydrogen sulphide $H_2S$, ammonia $H_3N$, and other similarly constituted bodies are found. Chlorine breaks up, as we have seen, those hydrogen compounds; hence, its great value for removing the unwholesome properties of the air in badly drained and ventilated buildings, etc.

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### SUMMARY.

**50.** Chlorine is a heavy, yellowish-green gas; it does not occur free in nature, but to a very great extent in combination with sodium. It may be obtained from either hydrochloric acid or sodium chloride; it is distinguished by its peculiar, strong odor; it is non-inflammable, but supports combustion; it is soluble in water, is a powerfully bleaching and strongly disinfecting agent, and decomposes water, with the evolution of free oxygen.

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### LABORATORY DIRECTIONS.

**51.** Chlorine rapidly attacks corks, which may be protected by dipping them into melted paraffin (*not* paraffin oil, but the solid substance melted in a small dish or basin).

The fumes produced by burning both phosphorus and antimony in chlorine are *poisonous;* should the student attempt to perform Experiment 27 or 28, he must be very careful not to inhale these fumes.

The reason why such care must be taken to have dry jars for sodium experiments (see Experiment 30) is that hot sodium accidently coming in contact with water explodes with great violence; be also careful that there is no water spilled about your experimenting table.

The student should at least perform Experiments 25 and 26,

and he should also prepare a bottle of chlorine water, which he may preserve for analytical work.

Wash all apparatus used for chlorine immediately it is done with; this applies especially to corks and rubber tubing; the latter should have a stream of water sent through it.

## COMPOUNDS OF CHLORINE WITH HYDROGEN.

### HYDROGEN CHLORIDE.

*Hydrogen chloride, or hydrochloric acid. Formula HCl. Molecular weight 36.37. Density 18.185. Specific gravity 1.26. Melting point —116°. Boiling point — 80° under atmospheric pressure. One liter of the gas at 0° weighs 1.63 grams (18.185 criths).*

**52. History.**—Hydrogen chloride is the only compound of chlorine with hydrogen. It is more generally known under the name of *hydrochloric acid*, or *muriatic acid.* It had been known to the alchemists under the name of *spirit of salts*, until Glauber, in the seventeenth century, gave it the name of muriatic acid, a name that has been derived from the Latin word *muria*, meaning "brine." The pure hydrogen chloride gas was first obtained by Priestley in 1772, though it was not till 1810 that its true composition was ascertained by Davy.

**53. Occurrence.**—Hydrochloric-acid gas is found in nature among the gases emanating from active volcanoes, and also occurs, though only sparingly, in spring and river waters in volcanic districts.

**54. Preparation.**—Hydrochloric acid is usually prepared by the action of sulphuric acid upon common salt:

$$\underset{\text{common salt}}{NaCl} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{hydrogen chloride}}{HCl} + \underset{\text{hydrogen sodium sulphate}}{NaHSO_4}$$

The operation is usually conducted, however, at a high temperature, when one molecule of sulphuric acid acts upon two molecules of sodium chloride, yielding neutral sodium sulphate and two molecules of hydrochloric acid:

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$

EXPERIMENT 35.—Twenty grams (18 cubic centimeters) of common salt, that has been previously dried in an oven, are placed in a so called Florence flask (see Fig. 28), to which has been fitted, by means of a perforated cork, a tube bent twice at right angles, to allow the gas to be collected by downward displacement. Thirty cubic centimeters

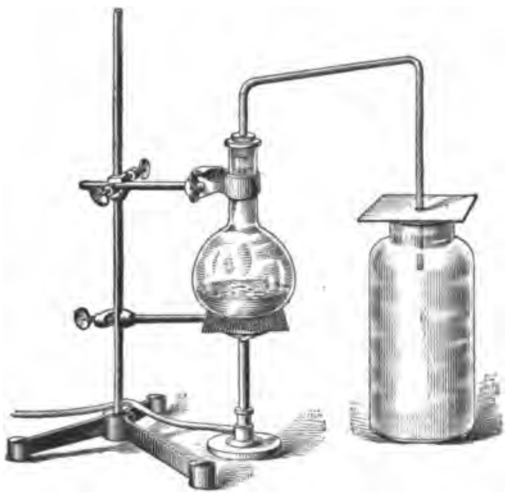

FIG. 28.

of strong sulphuric acid are poured upon the salt, and, the cork having been inserted, the flask is very gently heated, in order to promote the disengagement of the hydrochloric acid, which is collected in a perfectly dry bottle, the mouth of which, when full, may be covered with a glass plate smeared with a little grease. It is advisable to have the collecting bottle, while it is filled, covered with a perforated card.

It should be mentioned that common salt in powder froths to a very great extent with sulphuric acid; it is therefore mostly desirable to use pieces of so called rock salt, or to fuse the ordinary salt in a clay crucible till it has melted, and, after pouring the molten mass of salt into a cold iron

basin, break it up after it has thoroughly cooled, and then use it.

The collecting bottle will be known to be filled with the gas by the abundant escape of the dense fumes that hydrochloric-acid gas, itself transparent, produces by condensing the moisture of the air; for, since the gas is much heavier than air (its specific gravity being 1.26), it will not escape in any quantity from the bottle until the latter is entirely filled with it.

**55. Properties.**—Hydrogen chloride is a colorless, pungent, and acid gas; it fumes strongly in the air, is irrespirable, and extinguishes flame. Subjected to a pressure of 40 atmospheres at 10°, or of 2 atmospheres at $-70°$, it is condensed to a colorless, limpid liquid having a specific gravity of 1.27. The powerful attraction for water is one of the most remarkable properties of hydrogen chloride.

EXPERIMENT 36.—If a jar of hydrogen-chloride gas is closed with a glass plate and inverted under water, it will be found, on removing the plate, that the gas is absorbed with great rapidity, the water being forced up into the bottle by the pressure of the external air in proportion as the gas is absorbed.

The muriatic or hydrochloric acid of commerce is simply a solution of the gas in water, and may be recognized by its fumes and the peculiar odor that it evolves when exposed to the air.

One pint of water at a temperature of 4.5° absorbs nearly 480 pints of hydrochloric-acid gas, forming $1\frac{1}{3}$ pints of the solution, having a specific gravity of 1.21. The commercial hydrochloric acid has usually a bright-yellow color, which is due to the accidental presence of a small portion of ferric chloride $Fe_2Cl_6$.

**56. Composition of Hydrochloric Acid.**—The compositon of hydrochloric acid may be ascertained in a similar way to that of water; that is, by exposing its solution to electrolysis.

The standard apparatus for this purpose, which is the one

generally adopted for use upon the lecturer's table and in the laboratories of universities, is shown in Fig. 29. It is known as *Hofmann's apparatus for the decomposition of HCl*, and consists of three glass tubes connected at the bottom. Through *A* and *B* are passed rubber corks with carbon electrodes. (These are preferable to platinum electrodes, as nascent chlorine successfully attacks this metal.)

EXPERIMENT 37.—The apparatus is filled by means of the funnel *G* with concentrated hydrochloric acid to the level of the stop-cocks *C* and *D*, both being left open. A battery is connected with the apparatus by the wires *E* and *F*, and the current is turned on and allowed to pass through the apparatus for about an hour. The hydrogen rises rapidly from the negative electrode, but from the positive electrode, chlorine being soluble in water, little gas is evolved until the solution is fully saturated. At the end of about an hour, the stop-cocks *C* and *D* are turned off; equal volumes of gas should now collect in each of the tubes.

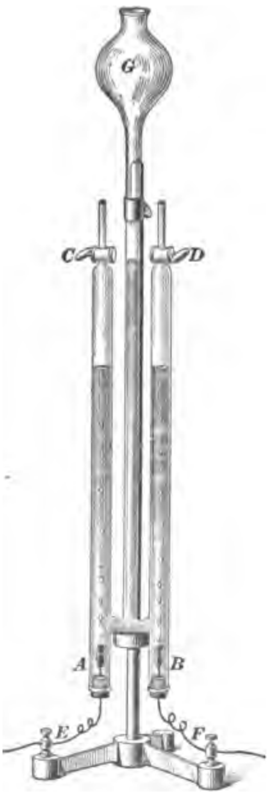

FIG. 29.

Should the chlorine be in too small a quantity, compared with that of hydrogen, it is a sign that the acid in that limb of the apparatus is not yet fully saturated. The chlorine gas may be readily recognized by its color; open the stop-cock of the tube containing the chlorine, and let the gas come in contact with a piece of wet litmus paper; it will then be noticed that the color of the litmus paper is very quickly changed to red.

Then, if a small gas jet is connected with the limb containing the hydrogen, by means of a piece of rubber tubing, and light is applied to the gas jet, after turning on the stop-cock, the issuing gas will be recognized by its inflammability.

Chlorine, like oxygen, is liberated from the electrode connected with the copper or platinum element of the battery. The following eight elements are similar in this respect, and

from their behavior with an electric current are called *negative: oxygen*, *chlorine*, *bromine*, *iodine*, *fluorine*, *sulphur*, *selenium*, and *tellurium*.

Another convenient apparatus is shown in Fig. 30.

EXPERIMENT 38.—Fit to the generating flask *A*, Fig. 30, containing salt and sulphuric acid, a U tube *B*, containing calcium chloride, for the purpose of drying the evolved gas. Connect this to a tube in which two bulbs *C* and *D* have been blown; into bulb *C* introduce some finely powdered manganese dioxide; the manganese dioxide should be perfectly dry; this is accomplished by warming it gently in an iron ladle over a Bunsen burner, or placing it on a sheet of tin on a stove for a

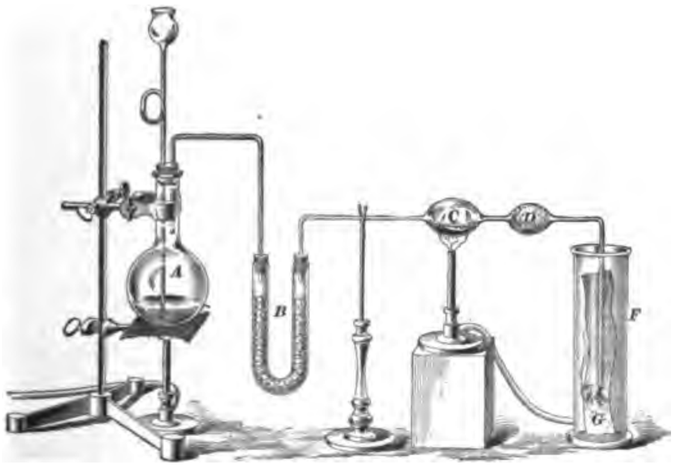


FIG. 30.

little while. Arrange a glass jar *F* to receive the escaping gas; place in it a sheet *G* of moist, blue litmus paper The hydrochloric acid evolved at once changes the color of the litmus paper. Apply heat to the bulb containing manganese dioxide, the hydrochloric acid is decomposed; water collects in the second bulb *D*, chlorine passes over into the jar *F*, and may be easily recognized by its odor and bleaching power.

**57. Uses.**—Hydrochloric acid is manufactured on an immense scale as a secondary product in the soda industry, and is used for various purposes in the chemical arts.

### SUMMARY.

**58.** As the valence of hydrogen is 1, hydrochloric acid is, and must be, the only existing compound of hydrogen and chlorine. It is easily prepared by the action of sulphuric acid on a chloride. Hydrochloric-acid gas is extremely soluble in water; it is colorless, and fumes on exposure to air. It has a sharp, pungent odor and sour taste; it is neither inflammable nor a supporter of combustion; it reddens litmus paper; it is composed of equal volumes of hydrogen and chlorine, as has been proved by analysis (see Experiment 37).

---

### LABORATORY DIRECTIONS.

**59.** The student should, if possible, perform Experiments 35 and 36. It is not absolutely necessary, in Experiment 38, that the tube containing manganese dioxide should have bulbs blown on it; a glass tube bent in the shape of a **W** will answer the purpose just as well.

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## OXIDES AND ACIDS OF CHLORINE.

**60.** It is interesting to notice that, though chlorine and hydrogen so readily unite, there is no method by which chlorine can be made to combine in a direct manner with oxygen, the compounds of these two elements having been obtained, so far, only indirectly. The fact that the more closely substances resemble one another in their chemical properties, the less will be their tendency to combine, is in this way beautifully illustrated. Both oxygen and chlorine are highly electronegative bodies, and consequently have a most powerful attraction for the electropositive hydrogen, while their mutual attraction is rather limited.

As chlorine may act as either a monad, a triad, a pentad, or a heptad, its oxygen compounds, theoretically, are four. These, with their corresponding acids, would be as follows:

| | | | |
|---|---|---|---|
| Hypochlorous oxide | $Cl'_2O$ | Hypochlorous acid | $HCl'O$ |
| Chlorous oxide | $Cl'''_2O_3$ | Chlorous acid | $HCl'''O_2$ |
| Chloric oxide | $Cl^{v}_2O_5$ | Chloric acid | $HCl^{v}O_3$ |
| Perchloric oxide | $Cl^{vii}_2O_7$ | Perchloric acid | $HCl^{vii}O_4$ |

All of these acids exist, but hypochlorous oxide or chlorine monoxide $Cl_2O$ is the only one of these oxides that has been prepared. Another oxide, chlorine dioxide $ClO_2$ or chlorine tetroxide $Cl_2O_4$ is known, however.

---

### HYPOCHLOROUS OXIDE AND ACID.

**61.** Hypochlorous oxide was discovered by Balard in 1834. It is of practical interest in connection with *chloride of lime*, *chloride of soda*, and other bleaching compounds. It may be prepared by passing dry chlorine gas over dry precipitated mercuric oxide, and condensing the product in a tube, packed in a mixture of salt and ice:

$$\underset{\text{mercuric oxide}}{HgO} + \underset{\text{chlorine}}{2Cl_2} = \underset{\text{mercuric chloride}}{HgCl_2} + \underset{\text{hypochlorous oxide}}{Cl_2O}$$

The hypochlorous oxide thus obtained is a blood-red liquid, which boils at 6°, evolving a yellow gas, about twice as heavy as atmospheric air, possessing a penetrating chlorine-like odor. It is decomposed with explosion by very slight causes, the heat of the hand having been known to cause its separation into its constitutents, when 2 volumes of the gas yield 2 volumes of chlorine and 1 volume of oxygen. Most substances that have any attraction for oxygen or chlorine, and that, consequently, raise the temperature of the gas by combining with a portion of its chlorine or oxygen, decompose this gas, and sometimes this decomposition occurs with explosive violence. This instability of hypochlorous oxide is then easily understood from the fact that it evolves heat in its decomposition; it is therefore an *endothermic* compound; i. e., one that could only be formed from its elements by the absorption of heat.

**62.** Hypochlorous oxide is absorbed by water in very large quantities, uniting with it to form *hypochlorous acid* $ClOH$, which retains the odor of the oxide and is a most powerful oxidizing and bleaching agent, since it is rather unstable and readily decomposes into $HCl$ and $O$. It erases writing ink immediately, and does not corrode the paper if it is carefully washed. Printing ink, which contains lamp-black and grease, is not bleached by hypochlorous acid, so that this solution is very useful for removing ink stains from books, engravings, etc.

**63.** The action of some metals and their oxides on a solution of hypochlorous acid is interesting and instructive. Iron seizes upon the oxygen, thus liberating chlorine; copper takes both the oxygen and chlorine; while silver, on the other hand, combines only with the chlorine, liberating the oxygen. This distinguishes the solution of $ClOH$ from chlorine water. Oxide of lead $PbO$ removes the oxygen, becoming plumbic peroxide $PbO_2$ and liberating chlorine; oxide of silver converts the chlorine into chloride of silver and liberates the oxygen:

$$Ag_2O + Cl_2O = 2AgCl + O_2$$

**64.** The salts of hypochlorous acid, commonly known as *hypochlorites*, are not known in a pure state, but are obtained in solution by neutralizing the solution of hypochlorous acid with bases. (Calcium hypochlorite has been obtained in crystals probably of the formula $Ca(OCl)_2, 4H_2O$ by evaporating a solution of chloride of lime *in vacuo* over sulphuric acid and potash.) These salts are very easily decomposed.

When a solution of hypochlorite is boiled, it becomes converted into a mixture of chloride and chlorate, as, for instance:

$$\underset{\text{potassium hypochlorite}}{3KClO} = \underset{\text{potassium chlorate}}{KClO_3} + \underset{\text{potassium chloride}}{2KCl}$$

This change is turned to practical account in the manufacture of chlorate of potassium.

Hypochlorites are prepared in the arts by exposing alkali hydroxides to the action of chlorine gas. With sodium hydroxide, the reaction occurring may be expressed as follows:

| $2NaOH$ | $+$ | $Cl_2$ | $=$ | $NaOCl$ | $+$ | $NaCl$ | $+$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|
| sodium hydroxide (or sodium hydrate) | | chlorine | | sodium hypochlorite | | sodium chloride | | water |

Hypochlorites are used in the arts to a very great extent as bleaching agents, the so called chloride of lime, which is probably a compound of calcium chloride and calcium hypochlorite, being manufactured for this purpose on an immense scale.

**65. Chloride of Lime ("calx chlorata"), or Bleaching Powder.**—Chloride of lime is the most important compound formed by hypochlorous acid. It is prepared on a large scale by passing chlorine gas into leaden boxes in which a quantity of moist slaked lime is exposed upon shelves. The temperature is not allowed to rise above 25°, which is insured by acting on the fresh lime with chlorine diluted by air. The lime absorbs nearly half its weight of chlorine, and forms a white powder, which possesses a peculiar odor, somewhat differing from that of chlorine.

The formula of chloride of lime is usually written $CaClOCl$.

The constitution of chloride of lime has not been actually ascertained. When the slaked lime [calcium hydrate $Ca(OH)_2$] is acted on by chlorine gas, the simplest reaction would be:

$$Ca(OH)_2 + Cl_2 = CaClOCl + H_2O$$

According to this equation, the chloride of lime would result from the replacement of one of the $OH$ groups by $Cl$, and the removal of the $H$ of the other as $H_2O$, this atom of $H$ being then replaced by $Cl$; but this would require the calcium hydrate to absorb nearly an equal weight of chlorine, where, as a matter of fact, the amount is only a little more than half this quantity. It is surmised that this deficiency is explained by the fact that a portion of the lime remains actually unattacked by the chlorine.

Practically, the constitution of chloride of lime is of less importance than that of the solution obtained by treating the chloride of lime with water, which is generally believed to contain *calcium hypochlorite* $Ca(OCl)_2$ and *calcium chloride* $CaCl_2$ with some *calcium hydrate* $Ca(OH)_2$, of which a quantity is left in the undissolved residue. The decomposition of chloride of lime by water should, then, be represented by the following equation:

$$2CaClOCl = CaCl_2 + Ca(OCl)_2$$

A solution of chloride of lime added to blue litmus exerts only a comparatively insignificant bleaching power, but if a little acid (sulphuric acid, for instance) is added, the blue color of the litmus will speedily disappear. This phenomenon may be explained by the fact that the acid liberates first the chlorine, which then in turn acts on the coloring matter. The following equation will completely demonstrate this fact:

$$\underbrace{Ca(OCl)_2 + CaCl_2}_{\text{solution of chloride of lime}} + \underbrace{2H_2SO_4}_{\text{sulphuric acid}} = \underbrace{2CaSO_4}_{\text{calcium sulphate}} + \underbrace{2H_2O}_{\text{water}} + \underbrace{2Cl_2}_{\text{chlorine}}$$

**66.** When chloride of lime is employed for bleaching purposes, the material to be bleached is first thoroughly washed and cleansed, in order to remove not only any grease but also the so called "*dressing*"; this is accomplished by boiling it in lime water, and in a weak solution of soda, after which it is immersed in a weak solution of chloride of lime. This, by itself, however, exerts only a very little bleaching action on the natural color of the fiber, and the material is, therefore, next immersed in a very dilute solution of sulphuric acid, when the coloring matter is so far altered as to become soluble in the alkaline solution in which the fabric is subsequently immersed, and a repetition of these processes, followed up by a thorough rinsing, generally perfects the bleaching.

**67.** The before mentioned property of acids to liberate chlorine from chloride of lime has been successfully applied

in calico printing for the purpose of producing white patterns on red ground.

The calico having been dyed with Turkey red, the pattern is printed upon it with a discharge consisting of an acid solution, such as tartaric, phosphoric, or arsenic, which has been thickened with gum. After being dried, the calico is passed through a bath consisting of a weak solution of chloride of lime. The acid contained in the discharge acts promptly on the chloride of lime, liberating the chlorine, which in turn bleaches the print without injuring the red ground of the calico.

The best bleaching powder in the market contains about 37 per cent. of chlorine (available chlorine).

**68.** Chloride of lime is one of the most convenient forms in which chlorine can be used for the purpose of disinfection and fumigation. A cloth saturated with a solution of chloride of lime and suspended in the air of a room answers very well for ordinary disinfecting purposes, because the carbonic-acid gas of the air causes slow evolution of hypochlorous acid, which is even a more powerful disinfectant than chlorine gas itself. In cases where a very rapid evolution of chlorine is required, as in dissecting rooms, clinics, and hospitals for contagious diseases, the bleaching powder is placed in a deep plate or basin and diluted sulphuric acid poured over it, or the powder is mixed with half its weight of alum, when a rapid and regular evolution of chlorine will ensue.

Chloride of lime is very liable to decompose when kept, evolving oxygen and becoming converted into calcium chloride, which attracts moisture eagerly and renders the powder deliquescent.

### CHLOROUS ACID.

**69.** When potassium chlorate is decomposed by dilute nitric acid in the presence of a reducing agent, such as arsenious oxide, sugar, or tartaric acid, an unstable yellowish-green gas that decomposes with explosive violence at about 57° is obtained. This gas dissolves in water quite readily, and

yields chlorous acid. It was formerly thought that this gas was chlorous oxide, but later investigation has shown it to be a mixture of chlorine dioxide and chlorine.

Chlorous acid is a very unstable compound. It unites slowly with bases, forming chlorites, which are also very unstable, and breaks up readily into chlorides and chlorates.

---

#### CHLORINE DIOXIDE OR TETROXIDE.

**70.** Chlorine dioxide $ClO_2$ or tetroxide $Cl_2O_4$ was discovered by Davy in 1814. It is often regarded as $O_2Cl^{v}\text{-}O\text{-}Cl'''O$, and this view is supported by the fact that it unites with water, forming chlorous and chloric acids; but at 10° its density is about 34, proving it to be $ClO_2$ at this temperature. It is possible, however, that at lower temperatures the double molecule exists. It may be regarded as intermediate between chlorous and chloric oxides. Water and the alkalies readily decompose the oxide into chlorous and chloric acids. It is obtained by the action of sulphuric acid on potassium chlorate. The salt is finely pulverized and is added in small quantities to sulphuric acid cooled to −10°. The pasty mass thus obtained is then introduced into a test tube, which is closed by a perforated cork in which a delivery tube is fitted, and is gently heated in a water bath; the gas thus disengaged is collected in dry jars by downward displacement. It is a dark, greenish gas, which, strongly diluted, has a sweetish odor and taste and is exceedingly oxidizing in its action. At −20° it condenses to an orange-red liquid. It explodes with great violence at 60°, often spontaneously. It is dangerous for the inexperienced experimenter to prepare.

EXPERIMENT 39.—The vigor of the action of chlorine tetroxide on combustibles may be tested by mixing together on a sheet of paper about ¼ cubic centimeter of very finely pulverized potassium chlorate, and an equal quantity of powdered sugar. Place this mixture on a piece of brick and touch it with a glass rod, previously dipped in strong sulphuric acid. The chlorine tetroxide thus set free causes a vivid combustion of the entire mass.

EXPERIMENT 40.—About 1 cubic centimeter of potassium chlorate is placed at the bottom of a tumbler filled with water, a couple of very small pieces of phosphorus added, and sulphuric acid allowed to come in contact with the salt, by means of a pipette. The phosphorus will at once take fire in the chlorine-tetroxide gas evolved, and will burn vividly.

---

### CHLORIC ACID.

**71.** Chloric acid $ClO_2(OH)$ or $HClO_3$ was first prepared by Gay-Lussac. It may be prepared by passing chlorine through a solution of potassium hydroxide, potassium chlorate and potassium chloride resulting, according to the equation:

| $3Cl_2$ | + | $6KHO$ | = | $KClO_3$ | + | $5KCl$ | + | $3H_2O$ |
|---|---|---|---|---|---|---|---|---|
| chlorine | | potassium hydroxide (caustic potash) | | potassium chlorate | | potassium chloride | | water |

By adding hydrofluosilicic acid to a solution of potassium chlorate, the latter is decomposed and the potassium precipitated as an insoluble silicofluoride, while chloric acid is found in the solution:

| $2KClO_3$ | + | $H_2SiF_6$ | = | $2HClO_3$ | + | $K_2SiF_6$ |
|---|---|---|---|---|---|---|
| potassium chlorate | | hydrofluo-silicic acid | | chloric acid | | potassium silicofluoride |

On evaporating the solution at a temperature not exceeding 38°, the chloric acid is obtained as a slightly yellow, syrupy acid with a pungent smell, of specific gravity 1.28, and containing about 40 per cent. of $HClO_3$. It cannot be preserved for any length of time, and at temperatures above 40° is decomposed into perchloric acid, water, chlorine, and oxygen:

$$8HClO_3 = 4HClO_4 + 2H_2O + 2Cl_2 + 3O_2$$

Chloric acid is one of the most powerful oxidizing agents; a drop of it will set fire to a piece of paper, and it oxidizes phosphorus (even the amorphous variety) with explosive violence.

Its salts, the chlorates, are also very active oxidizing agents. They are used for the preparation of oxygen, and in detonating and pyrotechnical mixtures.

**PERCHLORIC ACID.**

**72.** Perchloric acid $ClO_3OH$ or $HClO_4$ was discovered by Stadion in 1815, and has been recently more fully investigated by Roscoe, the author of a number of well known books on Chemistry; it is obtained by evaporating down, at a boiling heat, the solution of chloric acid obtained by decomposing potassium chlorate with hydrofluosilicic acid (see Art. **71**), when the chloric acid is decomposed into perchloric acid, water, chlorine, and oxygen, according to the equation:

$$8HClO_3 = 4HClO_4 + 2H_2O + 2Cl_2 + 3O_2$$

When the greater part of the water has been boiled off, the liquid may be placed in a retort and distilled. After the remainder of the water has passed over, it is followed by a heavy, oily liquid, which is $HClO_4,2H_2O$. If this is mixed with four times its volume of strong sulphuric acid and again subjected to distillation, the pure $HClO_4$ first passes over as a watery liquid. If the distillation should be continued, the oily $HClO_4,2H_2O$ distils over, and if this be mixed with the former and cooled, it yields silky crystals containing $HClO_4,H_2O$, which are decomposed at 110° into $HClO_4$, which may be distilled off, and $HClO_4,2H_2O$, which is left in the retort:

$$2HClO_4,H_2O = HClO_4 + HClO_4,2H_2O$$

Pure perchloric acid is a colorless, heavy, fuming liquid, having a specific gravity of 1.782 at 15°, which, however, soon becomes yellow from decomposition. It does not solidify at −35°. It cannot be kept for any length of time, though it is more stable than any other oxyacid of chlorine. When heated it undergoes decomposition, which is very often combined with explosion. Perchloric acid is an extremely powerful oxidizer; it burns the skin in a very serious manner, and sets fire to paper, charcoal, etc. with explosive violence.

This lack of stability belongs, however, solely to the pure acid. If water is added to it, heat is evolved and a diluted acid of much greater stability is obtained. Diluted perchloric acid does not even bleach, but reddens litmus in the ordinary way.

## THE HALOGEN GROUP.

**73.** The three elements, bromine, iodine, and fluorine, which will be considered in the subsequent articles, together with chlorine, which has been already fully described, constitute a group of elements known as *halogens*. As most acids are oxyacids, their corresponding salts must naturally contain oxygen; but the peculiarity of the halogens is that they yield salts which, owing to a direct union with the metals, are binary compounds. These salts, from their similarity to sea salt, are termed *haloid salts*, and hence the name *halogens* given to the elements from which, by combination with the elements, they are produced.

The relations of the members of this group to one another, which are very interesting, will be referred to after the different elements have been studied.

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## BROMINE.

*Symbol Br. Atomic weight 79.76. Density 79.76. Valence I, III, V, and VII. Specific gravity as gas 5.53; as liquid 3.18. Molecular weight 159.52. One liter of bromine vapor weighs 7.15 grams (79.76 criths).*

**74. History.**—Bromine was discovered by *Balard* in 1826, in the examination of *bittern*, which is the liquid remaining after the sodium chloride and some other salts have been made to crystallize by evaporating sea-water, which contains only about 1 grain of bromine per gallon in the forms of *bromide of magnesium* and *bromide of sodium*. Owing to its disagreeable odor, he gave it the name *bromine*, which is derived from the Greek word for "stench."

**75. Occurrence.**—Like chlorine, this element is never found uncombined in nature, but always in combination with other elements, such as sodium, potassium, and magnesium. It occurs in the waters of the springs of Kreuznach and Kissingen, in Germany, and during the last few years has been obtained from various saline springs in the United States and from the mother liquors of the salt works at Stassfurt, in Germany.

**76. Preparation.**—The first step in the preparation of bromine always is to separate the bromides from the chlorides with which they are to a greater or less extent associated. The solid salts are dissolved, and then concentrated by evaporation; the chlorides, being less soluble, first crystallize out and leave a mother liquor or bittern in which the bromides predominate. There are two reactions by which bromine may be obtained from this liquid. If chlorine be passed through the solution, bromine is liberated according to the following equation:

$$\underset{\text{magnesium bromide}}{MgBr_2} + \underset{\text{chlorine}}{Cl_2} = \underset{\text{magnesium chloride}}{MgCl_2} + \underset{\text{bromine}}{Br_2}$$

The bromine at first set free imparts a reddish-brown color to the solution. On shaking this with ether the bromine is dissolved, and its ethereal solution rises to the surface, and may be poured off from the watery layer underneath. On this ethereal solution being treated with potassium hydrate, its red color disappears, bromide and bromate of potassium being formed:

$$\underset{\text{bromine}}{3Br_2} + \underset{\text{potassium hydrate}}{6KHO} = \underset{\text{potassium bromide}}{5KBr} + \underset{\text{potassium bromate}}{KBrO_3} + \underset{\text{water}}{3H_2O}$$

The ether may be distilled off and recollected; the solid residue of bromide and bromate is ignited in order to decompose the bromate, which splits up into bromide and oxygen in the same manner as does potassium chlorate. In this way potassium bromide is obtained; the bromine may again be liberated by gently heating the bromide with manganese dioxide and sulphuric acid, when an analogous reaction occurs to that which takes place when a chloride is similarly heated:

$$\underset{\text{potassium bromide}}{2KBr} + \underset{\text{sulphuric acid}}{3H_2SO_4} + \underset{\text{manganese dioxide}}{MnO_2}$$

$$= \underset{\text{hydrogen potassium sulphate}}{2KHSO_4} + \underset{\text{manganese sulphate}}{MnSO_4} + \underset{\text{bromine}}{Br_2} + \underset{\text{water}}{2H_2O}$$

At times, the mother liquor, instead of being treated with chlorine, is evaporated down to dryness, and the residue mixed directly with sulphuric acid and manganese dioxide; but, in this case, as chlorides are always present in greater or less quantity, the bromine is liable to be contaminated with chlorine.

EXPERIMENT 41.—Take some potassium bromide, dissolve it in water, and pass from a generating flask some chlorine gas through the solution; notice that the color deepens through the liberation of the bromine. After some time, fill a test tube about two-thirds with the solution, and cool it thoroughly by holding it under a stream of cold water. Then add a little ether to the mixture, and, closing the tube firmly with your thumb, shake up the mixture thoroughly. After that, hold the tube still for a while, in order to allow the ether to collect on the surface of the liquid, but keep the mouth of the test tube all the time closed with your thumb until the two liquids have completely separated from each other. Notice that the ether leaves the watery solution almost colorless. (If the solution of bromine in ether is too concentrated, it falls to the bottom; in this case add a little more ether and shake again.) Pour off the ethereal solution; and, shaking up after each addition, add potassium-hydrate solution until the color entirely disappears. Evaporate the solution to dryness, and ignite; potassium bromide remains.

EXPERIMENT 42.—Pour into your retort a mixture of 3 grams (2 cubic centimeters according to your measuring glass) of manganese dioxide with 1½ grams (1½ cubic centimeters) of powdered potassium bromide, and set the retort on wire gauze on the ring of the support; pass its beak into a small receiver, which is kept cool by allowing it to rest in a dish with cold water. Take out the stopper of the retort and pour in about 20 cubic centimeters of strong sulphuric acid, replace the stopper at once, and apply heat gently to the retort. Dark-red fumes speedily fill the apparatus, and a heavy, dark-red liquid condenses in the receiver, which is bromine; when you have collected a little bromine, remove the lamp.

**77. Properties.**—Bromine, at ordinary temperature, is a dark, brownish-red, heavy liquid, so heavy that glass floats readily in it; it possesses an exceedingly penetrating and disagreeable odor, somewhat recalling that of chlorine. At a temperature of 63° it boils, and is converted into a deep-red vapor, which is about five and one-half times denser than air. Bromine freezes at −22°, becoming a gray crystalline solid, with a metallic luster. Water dissolves bromine but slightly,

33 parts of it dissolving, at a temperature of 15°, only 1 part of bromine. This solution possesses bleaching powers, but ot to such an extent as chlorine. In this, as in its other eactions, bromine and chlorine closely resemble each other, but bromine is the less active of the two, and is displaced from its compounds by chlorine. It is an active corrosive poison.

Bromine colors starch yellow; and a bromide in an aqueous solution precipitates silver from its solutions, as yellow silver bromide. It is used principally in photography and in medical science.

## IODINE.

*Symbol I. Atomic weight 126.54. Density 126.54. Valence I, III, V, and VII. Specific gravity as gas 8.74; as solid 4.95. Molecular weight, 253.08. One liter of iodine vapor at 0° weighs 11.37 grams (126.54 criths).*

**78. History and Occurrence.**—Iodine, as well as bromine and chlorine, is found in sea-water, but in considerably smaller quantities. Sodium iodide $NaI$ appears to constitute a portion of the necessary food of certain varieties of seaweed, which extract it from the sea-water and concentrate it in their tissues. On the coasts of Scotland and Normandy, large masses of seaweed were formerly burned in order to extract the soda they contained. The ash remaining after the seaweed has been burned, called *kelp* or *varec*, was dissolved in water, and the soda salts crystallized out. In the year 1811, Curtois, a soap manufacturer of Paris, being engaged in the manufacture of soda from kelp, obtained from the waste liquors a substance that possessed properties different from those of any form of matter with which he was acquainted. He turned this substance over to Clement, a French chemist, who satisfied himself that it was an entirely new and, so far, unknown substance. Davy and Gay-Lussac, in 1813, determined the elementary character of this substance, and named it *iodine*, derived from a Greek word, in allusion to the beautiful violet color of its vapor.

**79. Preparation.**—Iodine is prepared commercially on a large scale (the demand for this element having steadily increased on account of its employment in photography, etc.) from kelp, the collection and burning of which affords occupation to the poor inhabitants of some parts of the coasts of Ireland and Scotland.

The seaweed (the *Laminaria digitata*, or deep-sea tangle, seems to contain the most iodine) is spread out to dry, and is

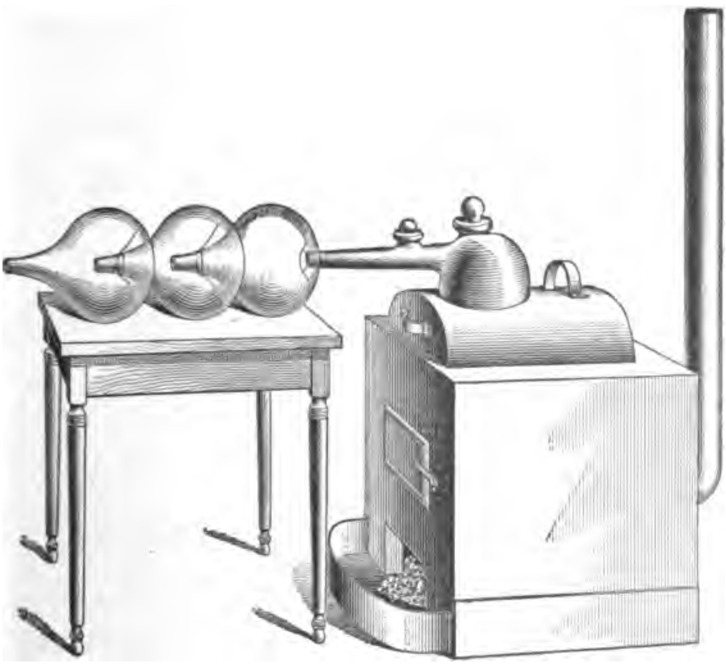

FIG. 31.

then burned in shallow pits at as low a temperature as possible, because the sodium iodide is converted into vapor and would be lost if the temperature were very high. The ash, which is left in a half-fused state, is broken into small pieces and treated with hot water, which dissolves about half of it, leaving a residue consisting of calcium carbonate and sulphate, sand, etc. The whole of the sodium iodide is

contained in the portion dissolved by the hot water, but is mixed with much larger quantities of sulphate, carbonate, thiosulphate, sulphide, and bromide of sodium, together with sulphate and chloride of potassium. A portion of the water is expelled by evaporation, when the sulphate and carbonate of sodium and chloride of potassium, being very much less soluble than the iodide of sodium, crystallize out. In order to decompose the thiosulphate and sulphide of sodium, the liquid is mixed with an eighth of its bulk of oil of vitriol, which decomposes these salts, evolving sulphur dioxide and hydrogen sulphide, with deposition of sulphur, and forming sodium sulphate, which is deposited in crystals. The liquor thus prepared is next mixed with manganese dioxide, and heated in an iron still with a leaden cover (Fig. 31), when the iodine is evolved in the form of a magnificent purple vapor, which condenses in the glass or stone receivers in the form of dark-gray scales, with a decided metallic luster. The liberation of the iodine is explained by the following equation:

$$\underset{\substack{\text{sodium}\\\text{iodide}}}{2NaI} + \underset{\substack{\text{manganese}\\\text{dioxide}}}{MnO_2} + \underset{\substack{\text{sulphuric}\\\text{acid}}}{2H_2SO_4}$$

$$= \underset{\substack{\text{sodium}\\\text{sulphate}}}{Na_2SO_4} + \underset{\substack{\text{manganese}\\\text{sulphate}}}{MnSO_4} + \underset{\text{water}}{2H_2O} + \underset{\text{iodine}}{I_2}$$

When no more iodine passes, some more manganese dioxide is added, and the bromine then distils. The quantity of bromine obtained is, approximately, one-tenth that of the iodine.

**80. Properties.**—The features of this element are well marked; at ordinary temperature it is a dark-colored (bluish-black) solid, possessing a metallic luster, which gives off small quantities of vapor of a splendid violet tint. Heated to about 115° iodine melts, and at about 200° boils, evolving a dense, violet, nearly black-appearing vapor, which is 8.74 times heavier than air, and is the heaviest vapor known; at 1,500°, however, the density of this vapor is reduced one-half.

The vapor possesses an odor resembling that of chlorine; this odor may already be noticed on smelling the substance at ordinary temperatures. Iodine is only very slightly soluble in water, to which it imparts a light yellowish-brown tint, 1 part of iodine requiring about 7,000 parts of water. Iodine dissolves in carbon disulphide—to which it imparts a violet tint, resembling the color of its vapor—as well as in alcohol, ether, and chloroform, the three last named substances forming with this element a brown solution. In chemical reactions iodine closely resembles chlorine and bromine, though it is less active than these two elements. It bleaches but faintly, if at all, in full sunlight, but combines directly with all metals to form iodides. Being less active than chlorine and bromine, iodine may be liberated from the iodides by the addition of either chlorine or bromine. On the other hand, the oxygen compounds of iodine are far more stable than those of chlorine and bromine.

Starch is the characteristic reagent for free iodine. It forms with it a deep-blue color, which is so intense that 1 part of iodine may be detected by it in 300,000 parts of water. This blue color vanishes on boiling, but reappears as the liquid cools. Iodine, when in a state of combination, does not give this reaction. The most delicate test for iodine is the purple-red color it produces when dissolved in carbon disulphide $CS_2$. One part of iodine in 1,000,000 parts of water may be detected in this way.

Iodine stains the skin yellow, but is not an active poison.

EXPERIMENT 43.—Prepare some starch solution by taking a small quantity (about 1½ to 2 cubic centimeters) and shaking it up with a test tube full of cold water. Immerse this tube in a beaker of boiling water until the starch gelatinizes, stirring it meanwhile. As soon as the thickening takes place, remove the tube and place it in another beaker, filled with cold water, until the starch solution has cooled to a normal temperature.

To a small portion of the starch solution thus obtained add a drop of solution of iodine in water; notice the blue color it obtains. Heat this blue-colored solution to boiling, and note the disappearance of the blue color, as well as the subsequent reappearance of it, as soon as the liquid cools.

To another portion of starch solution add some potassium iodide; notice that there is no change of color. Add next a drop of bromine dissolved in water; a blue color at once forms as a result of free iodine. Repeat the experiment, using chlorine water instead of the aqueous-bromine solution, and notice that the same effect is produced.

Add the solutions of bromine and chlorine to separate portions of the starch solution; neither of these produces the blue coloration.

**81. Uses.**—Iodine, both free and in combination, is extensively used in medicine, being particularly serviceable in glandular affections. It is also used extensively in photography and the manufacture of aniline colors.

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## FLUORINE.

*Symbol F. Atomic weight 19. Density 19. Valence I and III. Molecular weight 38. One liter at 0° weighs 1.7 grams (19 criths).*

**82. Occurrence and History.**—One of the most ornamental mineral substances, occurring abundantly in nearly every country, is *fluorspar*, sometimes called *Derbyshire spar* (fluoride of calcium). It is found in various shades of colors—blue, purple, violet, green, etc.—and again at other times, is nearly perfectly colorless.

The use of this mineral as a flux in smelting ores dates back to a very remote period, and from this use the name *fluor* appears to have been derived; but there exists no chemical record of its properties till about a century ago, when Margraf found his glass retort powerfully corroded in distilling this mineral with sulphuric acid, and Scheele, at about the same time, declared that it contained *lime* and *fluoric acid.* Though Scheele made the mistake to which analysts are continually liable, that is, to take the products for educts, his experiments, as they were later on perfected by Gay-Lussac and Thenard, deserve particular consideration.

**83. Preparation and Properties.**—The previously mentioned and well known mineral *fluorspar* is a compound

of fluorine with calcium $CaF_2$; from it hydrogen-potassium fluoride may be prepared, and, by the action of heat on this, anhydrous hydrogen fluoride is obtained and is electrolyzed. The liquid having been very carefully obtained pure, a little hydrogen-potassium fluoride is dissolved in it to improve its conducting power, and it is subjected to the action of the current in a **U** tube of platinum, down the limbs of which the electrodes are inserted; the negative electrode is a rod of platinum, while the positive one is made of an alloy of platinum and with 10 per cent. of iridium. The **U** tube is provided with stoppers of fluorspar and platinum delivery tubes for the gases, and is cooled to $-23°$. The gaseous fluorine evolved at the positive electrode may be freed from hydrofluoric acid $HF$ by the passage over dry potassium fluoride $KF$. The element is colorless and possesses the properties of chlorine, but much more strongly developed, and has an odor resembling that of hypochlorous acid.

It unites directly with hydrogen, even without the aid of light, and decomposes water readily. Sulphur, selenium, phosphorus, iodine, arsenic, antimony, silicon, boron, potassium, and sodium take fire in it spontaneously. Potassium chloride and potassium iodide are readily decomposed by fluorine, which liberates the chlorine and iodine. Organic substances are violently attacked and inflamed in it.

By igniting platinum fluoride, Moissan has obtained fluorine in an exceptionally pure form.

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## REVIEW OF THE HALOGENS.

**84.** Chlorine, bromine, iodine, and fluorine constitute, as will have been noticed, a closely allied group of elements, the members of which are characterized by possessing a remarkable similarity to one another. Chlorine, bromine, and iodine are much more closely connected with one another than with fluorine. Of these three first mentioned elements, chlorine is a gas, bromine a liquid, and iodine a solid at ordinary temperatures. Chlorine is yellowish green, bromine vapor is brown, and iodine vapor is purple. All of them

exist in the solid, liquid, and gaseous state, and change from one to either of the other states at temperatures not far apart. The density of the series increases, with chlorine as the lowest and iodine as the highest, while the chemical activity diminishes with the increase in density. Fluorine has a lower atomic weight than chlorine, and possesses greater chemical activity. The salts of these elements, frequently called *haloid salts*, are very much alike; those of the same metals commonly crystallize in the same form.

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### SUMMARY.

**85.** The group of elements termed halogens consists of chlorine, bromine, iodine, and fluorine.

Bromine is a dark-red liquid, evolving vapor of the same color. It occurs in sea-water, and is obtained from the bromides by action of sulphuric acid and manganese dioxide. It is similar in general behavior to chlorine, though less active; it may be displaced from its compounds by chlorine.

Iodine is a bluish-black solid with metallic luster, which, when warmed, evolves violet-colored vapors. It is found in the ashes of seaweeds, and is obtained by treatment with sulphuric acid and manganese dioxide. Iodine also resembles chlorine to a certain extent, but is even less active than bromine. Iodides are decomposed by either free bromine or chlorine. Iodine is characterized by imparting a deep-blue color to starch solution, but only possesses this property when in the free state.

Fluorine is so active that it has been, until recently, practically impossible to obtain it in the free state; it readily attacks glass vessels and decomposes water.

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### LABORATORY DIRECTIONS.

**86.** Remember that ether is very inflammable, and that it evolves vapor with very great rapidity; the vapor mixed with air is highly explosive; great care should, consequently,

be exercised in bringing a light near ether. Small quantities only should be used at a time. A so called store bottle should be kept, and a small one, say a 1-ounce or a $\frac{1}{2}$-ounce bottle, filled from it when required, in a room where there are *no* lights burning.

Bromine possesses an overpowering smell; be very careful to get as little of it as possible in your room or laboratory.

In making a starch solution, take care not to have it too thick; it should be sufficiently thin to pour out like oil.

## HYDROGEN COMPOUNDS OF BROMINE, IODINE, AND FLUORINE.

### HYDROGEN BROMIDE, OR HYDROBROMIC ACID.

**87.** Hydrobromic acid *HBr* possesses a molecular weight of 80.76 and a density of 40.38. The most instructive method

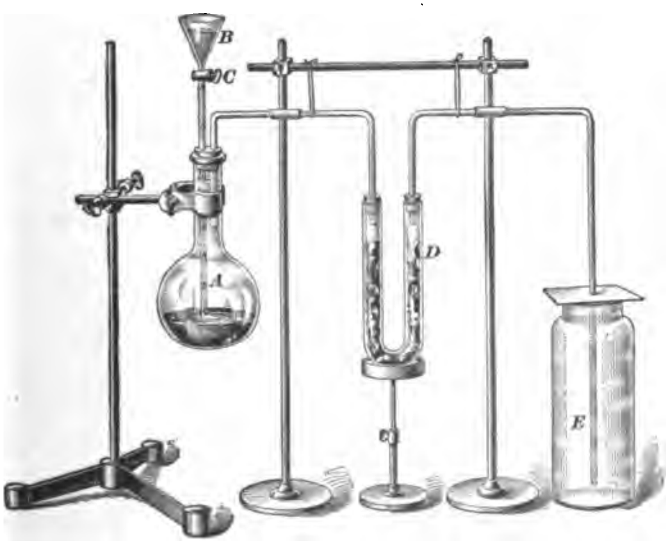


FIG. 32.

of preparing hydrobromic acid consists in attacking phosphorus by bromine in the presence of water, when phosphorus pentabromide is formed according to the equation:

| $P_4$ | + | $10Br_2$ | = | $4PBr_5$ |
|---|---|---|---|---|
| phosphorus | | bromine | | phosphorus pentabromide |

This is decomposed by the water as fast as it is formed, yielding phosphoric and hydrobromic acids:

| $PBr_5$ | + | $4H_2O$ | = | $H_3PO_4$ | + | $5HBr$ |
|---|---|---|---|---|---|---|
| phosphorus pentabromide | | water | | phosphoric acid | | hydrobromic acid |

EXPERIMENT 44.—To produce hydrobromic acid, the apparatus shown in Fig. 32 is required. 20 grams of red phosphorus are introduced into flask $A$ and are covered with 40 cubic centimeters of water. 120 grams (40 cubic centimeters) of bromine are allowed to fall, drop by drop, from a funnel $B$, which is provided with a glass stop-cock $C$ into the flask. The hydrogen bromide is passed through a U tube $D$ containing a mixture of small pieces of glass and moist red phosphorus, to absorb bromine, and is collected by downward displacement in the bottle $E$. After a little while the flask $A$ may be gently heated.

Hydrobromic acid is very similar to hydrochloric acid; it is a colorless acid gas, fuming strongly in moist air, and very soluble in water. It liquefies at $-73°$, and the liquid freezes at a temperature of $-120°$.

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### HYDROGEN IODINE, OR HYDRIODIC ACID.

**88.** Hydriodic acid $HI$ has a molecular weight of 127.54 and a density of 63.77. It is prepared by acting on phosphorus with iodine in the presence of water. The reactions are analogous to those that take place when hydrobromic acid is prepared in the same way, and may be expressed in one equation as follows:

$$P_4 + 10I_2 + 16H_2O = 4H_3PO_4 + 20HI$$

Or, if a smaller proportion of iodine is used, the reaction may be expressed thus:

$$P_4 + 6I_2 + 12H_2O = 4H_3PO_3 + 12HI$$

EXPERIMENT 45.— 6.5 grams of potassium iodide are dissolved in 30 cubic centimeters of water in a retort, as shown in Fig. 33, and 13 grams of iodine are added; when this has dissolved, .65 gram of amorphous phosphorus is introduced, and the mixture heated very gradually, the evolving gas being collected by downward displacement

in stoppered bottles, which should be right handy, as the gas evolves with great rapidity. The above given quantities will fill about four pint bottles of the gas.

**89.** Hydriodic acid, like hydrobromic acid, is a colorless gas, with a specific gravity of 4.41; it has an acid reaction, and fumes in the air. It easily condenses to a liquid by a pressure of 4 atmospheres at 0°; the liquid thus obtained,

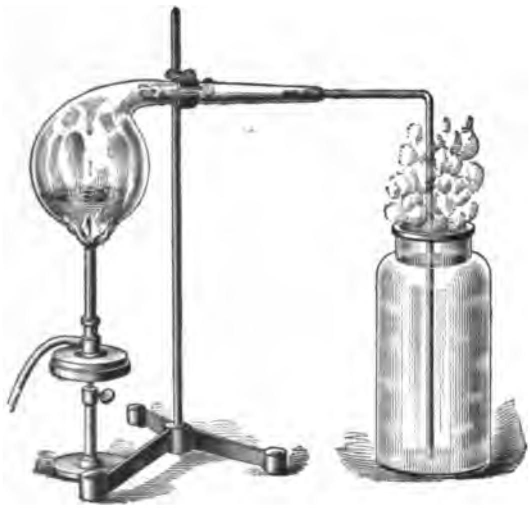

FIG. 83.

when subjected to $-51°$, freezes to a clear, ice-like solid. It is as soluble in water as hydrogen chloride, yielding, at 0°, a solution of specific gravity 1.99. An aqueous solution of hydriodic acid is most conveniently prepared by passing hydrogen-sulphide gas through water in which iodine is suspended. The principal reaction taking place may be expressed by the equation:

$$2H_2S + 2I_2 = 4HI + S_2$$

The separated sulphur is filtered off and the solution boiled to expel the excess of hydrogen sulphide. By this method it is, however, impossible to obtain a solution of hydriodic acid of greater specific gravity than 1.57.

Hydriodic acid differs, to a great extent, from hydrochloric

and hydrobromic acids in being decomposed by exposure to air, and particularly to light, its hydrogen being oxidized and iodine separated, which dissolves in the liquid and renders it brown.

This tendency of the hydrogen of hydriodic acid to oxidize, i. e., to combine with oxygen, makes this acid a powerful *reducing agent*. In organic chemistry, hydriodic acid is very frequently employed for introducing hydrogen into a compound; for instance, by heating benzene with hydriodic acid, the benzene may be made to take up 6 atoms of hydrogen: $C_6H_6 + 6HI = C_6H_{12} + 3I_2$. Since the attraction of iodine for hydrogen is so feeble, metalepsis does not occur between this halogen and hydrocarbons.

The circumstance that the organic compounds containing iodine are, as a rule, much less volatile and consequently more manageable than those of chlorine and bromine, leads to the extensive use of this element in researches on organic substances.

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### HYDROFLUORIC ACID.

**90.** Hydrofluoric acid $HF$ has a molecular weight of 20 and a density of 10. It is the most important compound of fluorine; it is prepared either by the action of sulphuric acid on calcium fluoride, calcium sulphate and hydrogen fluoride resulting, according to the equation:

$$\underset{\text{calcium fluoride}}{CaF_2} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{calcium sulphate}}{CaSO_4} + \underset{\text{hydrofluoric acid}}{2HF}$$

or by heating dry potassium-hydrogen fluoride $KHF_2$ to redness in a platinum still. The hydrofluoric acid thus obtained is a colorless liquid that boils at 19° and has a specific gravity of .985 at 12°. It solidifies at $-102°$ and melts again at $-92°$. Hydrofluoric acid has a most pungent, irritating odor, which, when inhaled in even small quantities, causes serious irritation of the lungs. The acid itself corrodes the skin powerfully when brought in contact with it, and creates painful ulcers.

The action of hydrofluoric acid on metals and their oxides

is very powerful; it dissolves all ordinary metals except gold, silver, platinum, mercury, and lead, but has only little action on magnesium.

The characteristic property of hydrofluoric acid, by which it becomes useful to the chemist in the laboratory as well as in the arts, is its power of dissolving silica. When a mixture of powdered sand and flint is digested in a leaden or platinum vessel with hydrofluoric acid, it is slowly dissolved, and, if the solution is then evaporated, the whole of the silica will be found to have disappeared in the form of gaseous silicon tetrafluoride:

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

If the silica is combined with a base, the metal will be left as a fluoride decomposable by either sulphuric or hydrochloric acid. These facts render hydrofluoric acid a very valuable agent in the analysis of the numerous silicates that resist the action of other acids.

The corrosion of glass and the usefulness of hydrofluoric acid for etching glass will now be readily understood. Ordinary glass consists of silicate of sodium or potassium combined with silicate of calcium or lead. The hydrofluoric acid attacks and removes the silica, and thus eats its way into the glass.

Experiment 46.—Warm a piece of glass and coat it with wax by letting a little melt on the surface and draining off the excess. When the wax has become cool and hardened, write on this coating with a pin. Mix in a small leaden dish some powdered fluorspar and concentrated sulphuric acid. Warm *very gently*; pungent fumes are evolved. Place the glass plate, with its written-on face downwards, on the top of the dish, and let it thus remain for from 5 to 6 minutes. Then remove the plate, clean it from the wax by gently heating it, and you will find that your original writing is permanently etched into the glass.

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### LABORATORY DIRECTIONS.

**91.** Experiment 44 cannot be performed by the student in an ordinary room, owing to the overpowering odor of bromine, and should be confined to a laboratory provided with a so called *stink closet*.

Hydrofluoric acid is exceedingly corrosive; great care must therefore be taken that none of it gets on the skin or is inhaled.

## OXIDES AND ACIDS OF BROMINE AND IODINE.

**92.** The analogy of bromine and iodine to chlorine is shown also in the similarity of their oxides and acids to those of chlorine. Theoretically, the series is the same, but practically only a few members of it have been thus far obtained.

Only the following bromine compounds are known:

| | |
|---|---|
| Hypobromous acid | $HBr'O$ |
| Bromic acid | $HBr^{v}O_3$ |
| Perbromic acid | $HBr^{vii}O_4$ |

and only those of iodine, given below, have been prepared:

| | |
|---|---|
| | Hypoiodous acid $HI'O$ |
| Iodic oxide $I_2^{v}O_5$ | Iodic acid $HI^{v}O_3$ |
| Periodic oxide $I_2^{vii}O_7$ | Periodic acid $HI^{vii}O_4$ |

### HYPOBROMOUS ACID.

**93.** Hypobromous acid $HBrO$ may be obtained in solution by shaking mercuric oxide with water and bromine. The solution thus obtained is very unstable, decomposing, especially when heated, with liberation of bromine and formation of bromic acid $HBrO_3$. W. Dancer has obtained this acid by the action of bromine on silver oxide suspended in water:

$$\underset{\text{bromine}}{2Br_2} + \underset{\text{silver oxide}}{Ag_2O} + \underset{\text{water}}{H_2O} = \underset{\text{silver bromide}}{2AgBr} + \underset{\text{hypobromous acid}}{2HBrO}$$

In this process it is necessary to operate very rapidly and avoid the contact of an excess of silver oxide with the hypobromous acid, as the latter would be destroyed by the oxide with the evolution of oxygen:

$$2HBrO + Ag_2O = 2AgBr + H_2O + O_2$$

The solution of hypobromous acid possesses a yellow color, and exhibits a bleaching power analogous to that of hypochlorous acid.

### BROMIC ACID.

**94.** Bromic acid $HBrO_3$ may be obtained, according to Kämmerer, by the action of chlorine on bromine in the presence of water:

$$5Cl_2 + Br_2 + 6H_2O = 10HCl + 2HBrO_3$$

The hydrochloric acid is driven out by evaporation, and bromic acid remains in the form of a liquid that cannot be concentrated to a syrupy liquid without partial decomposition.

### PERBROMIC ACID.

**95.** Perbromic acid $HBrO_4$ has been obtained, by decomposing perchloric acid with bromine, as a colorless, oily liquid, which is relatively stable, as are the corresponding chlorine and iodine acids.

### IODIC ACID.

**96.** Iodic acid $HIO_3$ is the most important compound of the bodies mentioned in Art. **92.** It is most conveniently prepared by boiling iodine with strong nitric acid in a long-necked flask, when it is dissolved in the form of iodic acid, which is left, on evaporating the nitric acid, as a white mass. This may be purified by dissolving in water and crystallizing, when the iodic acid forms white hexagonal tablets, which have the composition $HIO_3, H_2O$. When heated to 130° it loses its water of crystallization, and at about 180° it is decomposed into water and iodic oxide $I_2O_5$, which is, in turn, broken up into iodine and oxygen at a red heat.

## SULPHUR.

*Symbol S. Atomic weight 31.98. Density at 1,000°, 31.98. Valence II, IV, VI. Specific gravity of native crystals 2.05. Molecular weight at 1,000°, 63.96. One liter of sulphur vapor at a temperature of 1,000° weighs 2.86 grams (31.98 criths).*

**97. Occurrence.**—Sulphur has been known from the remotest times, and is a widely distributed element. In the neighborhood of volcanoes it occurs plentifully in the free state. It occurs as hydrogen sulphide $H_2S$ in many mineral springs, and very abundantly in combination with metals in various ores known as sulphides; and also in combination with oxygen and a metal as sulphates.

Of the first class, the most abundantly occurring are:

| | |
|---|---|
| Iron pyrites ........ | Iron disulphide $FeS_2$ |
| Copper pyrites...... | Sulphide of iron and copper $Cu_2S,Fe_2S_3$ |
| Galena............. | Sulphide of lead $PbS$ |
| Blende............. | Sulphide of zinc $ZnS$ |
| Crude antimony..... | Sulphide of antimony $Sb_2S_3$ |
| Cinnabar........... | Sulphide of mercury $HgS$ |

The most prominent sulphates are:

| | |
|---|---|
| Gypsum............ | Sulphate of calcium $CaSO_4,2H_2O$ |
| Heavy spar......... | Sulphate of barium $BaSO_4$ |
| Celestine........... | Sulphate of strontium $SrSO_4$ |
| Kieserite........... | Sulphate of magnesium $MgSO_4,7H_2O$ |
| Glauber's salt....... | Sulphate of sodium $Na_2SO_4,10H_2O$ |

Sulphur, as sulphate, forms an essential part of the animal tissues as a constituent of albumin, fibrin, etc., and it exists, also, to a considerable extent, in the tissues of vegetables and plants; its compounds cause the peculiar odor of cruciferous and alliaceous plants, such as garlic, mustard, etc.

Our chief supply of sulphur is drawn from Sicily, which furnishes about 80,000 tons annually. It is found there in large beds of blue clay in an uncombined state, but also very often associated with magnificent crystalline masses of strontium sulphate. The districts in which sulphur is found are mostly volcanic, and those that border the Mediterranean are particularly rich. Sulphur has also been found in Iceland and New Zealand.

**98. Preparation.**—The commercial sulphur is the native material in a purified state; and, as the native sulphur is commonly distributed in veins through masses of gypsum and

celestine, these impurities have to be separated from the sulphur by heat. This is accomplished by placing the native material in a row of earthen jars ($A$, Fig. 34), heated by a

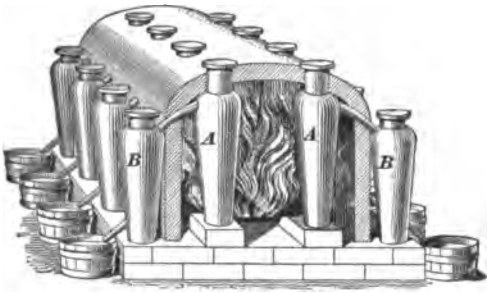


FIG. 34.

long furnace, and provided with narrow tubes, which convey the sulphur vapor into a second row of jars $B$, and which,

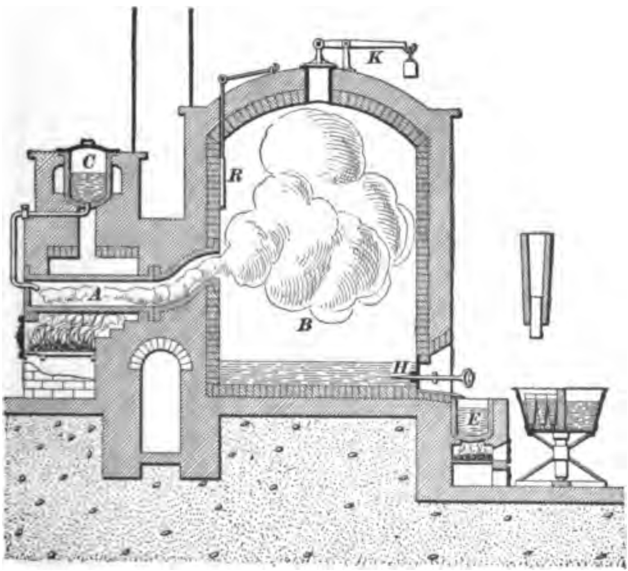


FIG. 35.

standing outside of the furnace, act as receivers, and condense the sulphur vapor into the liquid state, and from which it then flows out into pails of water.

The sulphur thus obtained is exported as *rough sulphur*, and contains between 3 and 4 per cent. of earthy impurities. In order to separate these, it must be redistilled. This redistilling, or, more exactly, refining process, is conducted in an apparatus that is shown in Fig. 35. A cast-iron cylinder *A* receives the melted sulphur from a tank *C* heated by the waste gases of the furnace. This sulphur vapor enters a large brick chamber *B*, the floor of which is slightly inclined, so that the condensed liquid sulphur may flow toward a tap *H*, which can be opened when necessary. A damper *R*, which is regulated through a chain attached to it, permits the closing or opening of the cylinder *A*. The brick chamber *B* is provided with a safety valve *K*, which permits the escape of the expanded air.

At first, when the walls of the brick chamber are still cold, the sulphur vapors condense in the form of a fine powder, known in commerce as *flowers of sulphur;* but afterwards, when the walls of the chamber become thoroughly heated, the sulphur vapors condense to a liquid, and on opening the tap *H* this is drawn off into a vessel *E*, and ladled into cylindrical molds, where it soon solidifies again, thus forming the commercial product commonly known as *roll brimstone*.

**99. Properties.**—In its ordinary form sulphur has a characteristic lemon-yellow color. It is insoluble in water; it may be called tasteless, but possesses a faint odor. The rolls of sulphur are of an extreme brittleness, and, as it is at the same time a very bad conductor of heat, the warmth of the hand is quite frequently sufficient to cause a roll of sulphur to fall to pieces when held. This phenomenon may be explained by the fact that roll sulphur, when freshly made, consists of a mass of oblique prismatic crystals, but, after being kept for some time, it consists of octahedra. This change in the structure of the mass, taking place when its solid condition prevents the free movement of the particles, gives rise to a state of internal tension and causes this extreme brittleness. The warmth of the hand causes an unequal expansion of the roll of sulphur; or, in other words,

it causes an increased movement of its particles in that part of the roll of sulphur which is directly exposed to the human heat, which results in a breaking up of the mass. Sulphur melts at a temperature of 113° to a limpid, yellow liquid, which, if allowed to cool slowly, deposits long, prismatic, needle-like crystals. These are at first perfectly transparent, but after a short time become entirely opaque, through each breaking up into a number of minute rhombic octahedral crystals. Though the external form is retained, little coherence remains.

If sulphur is dissolved in carbon disulphide, and the liquid then allowed to evaporate, the sulphur is obtained in octahedral crystals of the rhombic system. These are permanent in air, and the form is that in which native sulphur crystals occur.

EXPERIMENT 47.—Take an iron ladle, or a clay crucible, about 3½ inches high, fill it with sulphur, and heat it very gently over a small flame, taking care that the sulphur and the flame do not come in contact. As soon as the whole of the sulphur is melted, remove the Bunsen burner; as it cools, a crust forms over the surface, crystals being seen to shoot out from the side. Immediately this crust is formed, bore two holes through it with a piece of red-hot iron wire close to the edges and opposite each other; pour out the sulphur that still remains melted, and then cut with a knife the upper crust and remove it. It will be noticed that the interior is one mass of long, transparent needles, or prisms. Set the mass aside for five or six days and then observe that the crystals have entirely lost their transparency.

EXPERIMENT 48.—Shake up some flowers of sulphur with a little carbon disulphide, so as to form a saturated solution, in a test tube. Decant off the clear liquid and filter into an evaporating basin. Set aside and allow the carbon disulphide to evaporate spontaneously. A residue of more or less transparent octahedral crystals of sulphur will be found to remain in the basin.

These two experiments prove that there are two distinct forms in which sulphur crystallizes, the one from fusion, the other from solution. The latter is permanent, while the former is unstable, gradually changing into the latter.

In addition to these two varieties there is another one still, known as *plastic sulphur*, possessing properties that widely differ from those of either. If, instead of allowing the

limpid, yellow liquid, produced as a result of melting sulphur (obtained in Experiment 47 just before withdrawing the Bunsen burner), to cool, the application of heat is continued, a remarkable series of changes ensues. The color gradually darkens as the temperature rises; at the same time the liquid becomes thicker, until at a temperature of 180° the mass is almost black, and so viscid that the vessel may be inverted without the sulphur running out. With a further increase in temperature, the sulphur again becomes liquid, but remains of a much thicker consistency than it possessed when first melted. If, while in this state, it is poured into water, a soft, rubber-like, plastic mass is obtained. The difference between this variety and the common brittle form of sulphur is very striking. In a few hours, however, it loses its tenacity and becomes again opaque and brittle.

Either variety of sulphur melts when heated to 113°, becoming always a yellow, limpid liquid. As the temperature rises it becomes viscid, until, between 200° and 250°, the vessel may be inverted without any of the sulphur running out; it then becomes liquid again and at 440° boils. The vapor density of sulphur was for a time considered anomalous, being, at 500°, 96, till Bineau showed that at 1,000° it became 31.98. It is, therefore, assumed that at 500° the sulphur molecule must be hexatomic, while, if further heated to 1,000°, it becomes diatomic.

When heated to 260° in the air, sulphur takes fire and burns with a pale-blue flame emitting a suffocating odor, the reaction that takes place being represented by the following equation:

$$\underset{\text{sulphur}}{S_2} + \underset{\text{oxygen}}{2O_2} = \underset{\substack{\text{sulphur}\\\text{dioxide}}}{2SO_2}$$

Sulphur is an active supporter of combustion; many metals take fire readily in its vapor, and, burning actively, combine with it. Silver and sulphur combine at ordinary temperatures, giving the metal a black coating of silver sulphide.

**100. Tests.**—In the free state, sulphur may be easily recognized by its color, by its volatility when heated, and by

its characteristic odor when burned. Combined, as a sulphide, it blackens paper moistened with a solution of lead acetate.

**101. Uses.**—Sulphur finds an extensive employment in the arts and various manufacturing processes, such as the manufacture of sulphuric acid, gunpowder, in the vulcanization process of India rubber, for bleaching straws, woolens, etc.

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### SUMMARY.

**102.** Sulphur is found native in volcanic districts, uncombined, and also combined as sulphides and sulphates. It is purified by distillation; is a lemon-yellow, brittle solid; it occurs in two crystalline forms, one of which is unstable; it may also be obtained in the plastic form by heating nearly to the boiling point and cooling it suddenly by pouring it into cold water. It is volatile when heated and highly inflammable. It combines with most metals and with many of the metalloids.

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### LABORATORY DIRECTIONS.

**103.** To succeed in obtaining sulphur crystals by solidification of the melted body (see Experiment 47), bore the holes through the crust *immediately* it forms, and drain the melted sulphur away *completely*.

In pouring sulphur from a test tube, there is danger of the tube being cracked, unless its upper part is thoroughly heated. The safest plan is, before pouring, to boil the sulphur until the whole tube is filled with vapor; by this means the tube becomes uniformly heated and the danger of cracking is reasonably removed; be very careful, nevertheless, to so hold the test tube that, in the event of its breaking, none of the sulphur falls on your hand; boiling sulphur produces very painful and disagreeable burns. The liquid will probably take fire as it leaves the test tube; this, however, is of no importance. Should any fall on the bench, throw a little water on it at once.

## SULPHUR AND HYDROGEN.

### HYDROGEN SULPHIDE.

*Formula $H_2S$. Molecular weight 33.98. Density 16.99. Specific gravity 1.177. One liter weighs 1.52 grams (16.99 criths).*

**104. History and Occurrence.**—Hydrogen sulphide, formerly generally known as *sulphureted hydrogen*, was discovered by Scheele in the year 1777. It occurs in certain volcanic gases, and is the essential constituent of the water of the so called *sulphur springs*. The best known of these are Sharon and Avon, in the United States; Harrowgate, in England; Aix-la-Chapelle, in Germany; and Bagnières, in France.

**105. Preparation.**—Hydrogen sulphide may be prepared by the direct union of its components; that is, by passing hydrogen into sulphur vapor.

EXPERIMENT 49.—Arrange a retort with its stem just dipping beneath the surface of the water in the pneumatic trough. Place some sulphur in the retort and heat to the boiling point. Withdraw the stopper from the tubulure of the retort, and insert a cork through which has been passed a glass tube of such a length as to nearly reach the surface of the melted sulphur. Through this tube pass hydrogen from a generating flask, and collect it as it escapes from the stem of the retort. The gas possesses the odor of rotten eggs, and a piece of paper moistened with a solution of lead acetate is blackened when plunged into the gas.

Hydrogen sulphide is commonly prepared for use in the laboratory by the action of dilute sulphuric acid on a sulphide, that of iron being usually chosen. The reaction goes on readily, without the application of heat, the iron displacing the hydrogen, and the sulphur and hydrogen uniting:

$$\underset{\text{ferrous sulphide}}{FeS} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{ferrous sulphate}}{FeSO_4} + \underset{\text{hydrogen sulphide}}{H_2S}$$

EXPERIMENT 50.—A few fragments of ferrous sulphide are placed in a bottle *A*, of the apparatus shown in Fig. 36, which is provided with a funnel tube for the addition of the acid and a bent tube for conducting the gas through a small quantity of water, to remove any ferrous sulphate that may be carried along by the evolved gas. From the second bottle *B* (wash bottle) the gas is conducted by a glass tube with a rubber joint, either down into a glass bottle, or into water, or any other liquid on which the gas is intended to act. The fragments of ferrous sulphide should be covered with enough water to fill the generating bottle about one-third, and strong sulphuric acid is slowly added

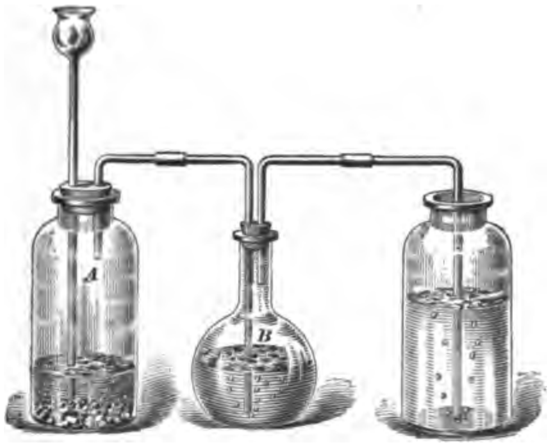


FIG. 36.

through the funnel, the bottle being shaken until effervescence is observed. An excess of strong sulphuric acid, however, stops the evolution of hydrogen sulphide by precipitating a quantity of white anhydrous ferrous sulphate, which coats the sulphide and defends it from the further action of the acid.

When no more gas is required, the acid liquid should be at once poured off, leaving the piece of ferrous sulphide at the bottom of the bottle for fresh generation when required.

The liquid acid, if set aside, will deposit green crystals of ferrous sulphate, having a composition of $FeSO_4,7H_2O$.

For the continuous preparation of hydrogen sulphide from ferrous sulphide and dilute sulphuric acid, in the larger laboratories, **Kipp's apparatus**, which is shown in Fig. 37, is very convenient. It consists of three glass bulbs, the two lower ones *A* and *B* being in a single piece, and the

upper one $C$ prolonged by a tube $D$ reaching to the bottom of the lower, being ground air-tight into the neck of the second. Through the tubulure $E$, the ferrous sulphide, in small fragments about the size of a chestnut, is introduced, the space between the tube and the side of the constriction being too narrow to let them drop into the bulb $A$. This tubulure $E$ is then closed by a cork, through which a glass stop-cock $F$ passes. The diluted acid (in the proportion of 1 part of acid to 9 parts of water) is poured through the safety tube $G$ and runs into the bulb $A$, and rises to overflow the iron sulphide in bulb $B$. If the stop-cock $F$ is open, the evolved gas escapes; but when this cock is shut, the pressure of the accumulating gas forces the liquid away from the sulphide down into the bulb $A$, and thence back into bulb $C$, thus stopping the action of further generating, and, at the same time, preserving a certain volume of hydrogen sulphide always ready when required. The acid, when saturated, is removed through the tubulure $H$.


FIG. 37.

**106. Properties.**—Hydrogen sulphide is a colorless gas, and has the disgusting odor of rotten eggs. It is

heavier than air, having a specific gravity of 1.177. Cooled to $-74°$, or submitted to a pressure of 17 atmospheres at 10°, it condenses to a colorless liquid of specific gravity of .9, which freezes to an ice-like mass at $-85°$. It is soluble in water, 1 volume of which dissolves 3 volumes at ordinary temperatures, and 4.37 volumes at 0°. The solution has a taste corresponding to the odor of the gas. It is inflammable and a non-supporter of combustion. Its reaction with blue litmus paper is weakly acid. It is easily decomposed by a temperature of 400°. It reacts with metals and their oxides to produce sulphides, setting hydrogen free in the first case, and water in the second. Hydrogen sulphide is exceedingly poisonous; according to Faraday, birds die in air which contains but $\frac{1}{1500}$ part of it, and dogs in that which contains but $\frac{1}{800}$.

**107. Tests.**—Hydrogen sulphide is easily detected by placing in it a piece of paper moistened with a solution of lead acetate; in this way it may be shown to exist in most specimens of coal gas, and in the gaseous exhalations from drains, cesspools, etc. With sodium nitroferrocyanide in alkaline solution, it strikes a deep-purple color.

**108. Acidity of Hydrogen Sulphide.**—The action of hydrogen sulphide on blue litmus paper shows that the gas possesses acid properties. These are, however, so feeble that, in the case of soluble sulphides, carbon dioxide is able to displace the hydrogen sulphide. The sulphides of all the metals are insoluble in water, with the exception of those of calcium, barium, strontium, magnesium, sodium, and potassium, and a few of the very rare metals. The insolubility of the other metallic sulphides affords the analyst a very valuable means of separating those metals from the group mentioned above. Whenever the compounds containing elements that, by their union, are capable of forming an insoluble compound, are brought together, that compound, as a rule, will be formed; so that, although hydrogen sulphide is rather a weak acid, it is thus able to displace stronger ones

from many metals. A current of hydrogen sulphide passed through a solution of copper chloride precipitates copper sulphide, according to the equation,

$$\underset{\text{copper chloride}}{CuCl_2} + \underset{\text{hydrogen sulphide}}{H_2S} = \underset{\text{copper sulphide}}{CuS} + \underset{\text{hydrochloric acid}}{2HCl}$$

and this although hydrochloric acid is so much more powerful in its action.

These sulphides have, in many cases, very characteristic colors, by which they may be readily recognized. They possess, further, the advantage of being divided into two distinct groups; namely, into one group that is soluble in dilute hydrochloric acid, and into another group that is insoluble in this agent.

EXPERIMENT 51.—Prepare a solution in separate test tubes of each of the following substances: *sodium arsenite*, *copper sulphate*, *antimony chloride*,* and *zinc sulphate;* acidulate these solutions by adding a few drops of hydrochloric acid to each, and pass hydrogen sulphide through each solution from the generating apparatus shown in Fig. 36. You have, of course, to be careful and wash the leading tube of the generating apparatus which dips into the solution each time before you introduce it into another.

You will in this way observe the following reactions:

$$\underset{\text{sodium arsenite}}{2Na_2HAsO_3} + \underset{\text{hydrogen sulphide}}{3H_2S} + \underset{\text{hydrochloric acid}}{4HCl}$$

$$= \underset{\text{sodium chloride}}{NaCl} + \underset{\text{water}}{6H_2O} + \underset{\text{arsenious sulphide}}{As_2S_3} \text{ (lemon yellow)}$$

$$\underset{\text{copper sulphate}}{CuSO_4} + \underset{\text{hydrogen sulphide}}{H_2S} = \underset{\text{sulphuric acid}}{H_2SO_4} + \underset{\text{copper sulphide}}{CuS} \text{ (black)}$$

$$\underset{\text{antimony chloride}}{2SbCl_3} + \underset{\text{hydrogen sulphide}}{3H_2S} = \underset{\text{hydrochloric acid}}{6HCl} + \underset{\text{antimony sulphide}}{Sb_2S_3} \text{ (orange)}$$

$$\left.\underset{\text{zinc sulphate}}{ZnSO_4}\right\} \text{In acid solution, } H_2S \text{ produces no precipitate.}$$

* Enough hydrochloric acid must be added to this during solution to prevent the separation of an insoluble compound, and keep the solution clear.

Introduce again into a clean test tube zinc-sulphate solution, but do *not* add hydrochloric acid, and you will obtain the following result:

$$\underset{\text{zinc sulphate}}{ZnSO_4} + \underset{\text{hydrogen sulphide}}{H_2S} = \underset{\text{sulphuric acid}}{H_2SO_4} + \underset{\text{zinc sulphide}}{ZnS} \text{ (white)}$$

If you add now to this a few drops of hydrochloric acid, you will find that the precipitate is immediately redissolved.

This series of experiments impresses on us that the sulphides thus produced are well defined salts, and a series of bodies of great importance.

Although sulphur is thus able to displace the metals from their compounds with chlorine, owing to the operation of the law mentioned in the beginning of this article, yet chlorine is capable of decomposing hydrogen sulphide very readily, the action being represented thus:

$$2H_2S + 2Cl_2 = S_2 + 4HCl$$

**109. Decomposition of Hydrogen Sulphide.**—The great affinity existing between hydrogen and chlorine leads to the decomposition of hydrogen sulphide, as has been shown in the last equation given in Art. **108.**

Free oxygen has no action on the dry gas, but in the presence of water, a slow oxidation takes place. Hence, an aqueous solution of hydrogen sulphide becomes turbid on exposure to the atmosphere, through the separation of sulphur and the formation of water, thus:

$$\underset{\text{hydrogen sulphide}}{2H_2S} + \underset{\text{oxygen}}{O_2} = \underset{\text{sulphur}}{S_2} + \underset{\text{water}}{2H_2O}$$

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## SUMMARY.

**110.** Hydrogen sulphide occurs free in the gases evolved from volcanoes, and combined in the waters of certain springs, known as sulphur springs. It is usually prepared by the action of sulphuric acid upon sulphides. It is soluble in water, a colorless gas with the disgusting smell of rotten

eggs, and is a non-supporter of combustion. By the action of chlorine it is decomposed. It possesses feeble acid properties; certain sulphides possess characteristic colors by which they may be readily recognized.

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### LABORATORY DIRECTIONS.

**111.** After the preparation of hydrogen sulphide, always wash out carefully the apparatus used before putting it away; otherwise a mass of crystals of iron sulphate may form. Any iron sulphide remaining unused should be washed and dried, and then returned to its proper bottle or box. There is sometimes some difficulty, when sulphide is taken that has been previously used, in getting the action to commence; there should always be a little fresh sulphide added as well. The difficulty also sometimes arises through the sulphuric acid being too strong.

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## OXIDES AND ACIDS OF SULPHUR.

**112.** Sulphur may unite with oxygen as a dyad, tetrad, and hexad, and, consequently, is able to form the following series of oxides and dibasic acids:

| | | | |
|---|---|---|---|
| Hyposulphurous oxide | $S''O$ | Hyposulphurous acid | $H_2S''O_2$ |
| Sulphurous oxide | $S^{iv}O_2$ | Sulphurous acid | $H_2S^{iv}O_3$ |
| Sulphuric oxide | $S^{vi}O_3$ | Sulphuric acid | $H_2S^{vi}O_4$ |

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### HYPOSULPHUROUS ACID.

**113.** Hyposulphurous oxide is not known, but hyposulphurous acid $H_2SO_2$ has been obtained by a German chemist named Schützenberger, by the reduction of sulphurous acid by means of zinc, according to the equation:

$$\underset{\text{zinc}}{Zn} + \underset{\text{sulphurous acid}}{2H_2SO_3} = \underset{\text{zinc sulphite}}{ZnSO_3} + \underset{\text{hyposulphurous acid}}{H_2SO_2} + \underset{\text{water}}{H_2O}$$

A yellow solution resulted which possessed a strong bleaching power, decolorizing litmus and indigo solutions readily.

The acid combines readily with oxygen and is a more active reducing agent than sulphurous acid. It is decomposed on standing in the air, producing sulphurous acid, water, and sulphur.

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## SULPHUROUS OXIDE.

*Formula $SO_2$. Molecular weight 63.9. Density 31.95. The weight of 1 liter is 2.86 grams (31.95 criths).*

**114. History and Occurrence.**—Attention to sulphurous oxide was first called by the alchemist Stahl, but not until 1774 did Priestley carefully investigate this compound and its properties. In nature, sulphurous oxide (or sulphur dioxide or sulphurous anhydride, according to different authorities) is but rarely met with; it exists in the gases issuing from volcanoes. Although constantly discharged into the air of towns by the combustion of coal (which always contains more or less sulphur), it is so easily oxidized and converted into sulphuric acid that no considerable quantity is ever found in the atmosphere.

**115. Preparation.**—Sulphurous oxide is uniformly the product of the combustion of sulphur in air or in pure oxygen, being formed thus:

$$S_2 + 2O_2 = 2SO_2$$

When needed for laboratory use it is generally prepared by heating sulphuric acid with metallic copper:

$$\underset{\text{sulphuric acid}}{2H_2SO_4} + \underset{\text{copper}}{Cu} = \underset{\text{copper sulphate}}{CuSO_4} + \underset{\text{water}}{2H_2O} + \underset{\text{sulphurous oxide}}{SO_2}$$

EXPERIMENT 52.— 20 grams (about 5¼ cubic centimeters according to your measuring glass) of copper clippings are heated in a Florence flask with 110 cubic centimeters of strong sulphuric acid, the gas being conducted by a bent tube down to the bottom of a dry bottle closed with a perforated card (see Fig. 28). Some time will elapse before the gas will evolve, for sulphuric acid acts on copper only at a high temperature; but when the evolution of the gas fairly commences it will proceed very rapidly, so that it is necessary to remove the flame from under the flask. The gas will contain a little suspended vapor of sulphuric acid, which makes it turbid.

**116. Properties.**—Sulphurous oxide is a very heavy, colorless gas, with a pungent, suffocating odor, resembling the odor of a burning sulphur match. It is more than twice as heavy as air, its specific gravity being 2.23. Cooled to – 10°, it condenses to a thin, colorless liquid with a specific gravity of 1.45, which freezes at – 76°.

EXPERIMENT 53.—Dry the gas evolved from the generating apparatus described in Experiment 52 and shown in Fig. 28, by passing it through concentrated sulphuric acid in a small wash bottle (see Fig. 38), and

FIG. 38.

then pass it through a spiral glass tube, which is inclosed in a vessel containing a mixture of crushed ice and salt, which mixture should be packed as closely as possible around the glass spiral. Let the end of the spiral dip into a test tube, which is also placed in some of the ice-and-salt mixture; as the gas passes through the spiral it is condensed, and collects in the test tube. When a little of the liquid has accumulated, pour it on the bulb of an alcohol thermometer, around which cotton wool has been wrapped; notice the great cold produced by rapid evaporation.

Heated to 1,200° under pressure, sulphurous oxide is decomposed, yielding sulphuric oxide and sulphur.

Sulphurous oxide is very easily absorbed by water, 1 volume of which dissolves at 0°, 68.86 and, at 20°, 36.22 volumes of the gas. The solution is believed to contain *hydrogen sulphite*, or *sulphurous acid* $H_2SO_3$, formed by the reaction:

$$H_2O + SO_2 = H_2SO_3$$

but this body has not been actually obtained in the free state.

Sulphurous oxide possesses the property of extinguishing flame. A taper is at once extinguished in a bottle of this gas.

One of the best methods of extinguishing burning soot in a chimney consists in passing up sulphurous-oxide gas, by burning a few grams of sulphur in a pan placed over the fire.

**117. Tests.**—Sulphurous oxide when free is at once detected by its pungent odor, and by its blackening action on paper moistened with a solution of mercurous nitrate. In combination as a sulphite, it evolves hydrogen sulphide when added to any solution evolving hydrogen.

**118. Uses.**—The principal uses of sulphurous oxide and sulphurous acid depend on their property of bleaching many animal and vegetable coloring matters. Although far less powerful bleaching agents than chlorine, they are preferred for bleaching silks, straw, wool, isinglass, baskets, etc., which would be injured by the great energy of chlorine.

The articles intended to be bleached are first moistened with water and then placed in a chamber where sulphurous-oxide gas is produced by the combustion of sulphur. Stains of fruit, red wines, etc. on linen are conveniently removed by sulphurous-acid solutions.

The property of sulphurous oxide and acid to stop fermentation and putrefaction has made these compounds valuable as disinfecting agents. This property is commonly called the *antiseptic* or *antizymotic* property of the compounds, and is turned into account, to use an every-day example, when casks for wine and beer are sulphured, in order to prevent the action of any substance contained in the pores of the wood, and capable of exciting fermentation, upon the fresh liquor to be introduced.

The salts of sulphurous acid (*sulphites*) are used in the manufacture of sugar to arrest fermentation. Clothes are sometimes fumigated with sulphurous-oxide gas in hospitals, police stations, etc. to destroy vermin and germs. The air of rooms in which people afflicted with contagious diseases have stayed is disinfected by burning sulphur in it, 4 pounds of sulphur being generally used for every 1,000 cubic feet of space.

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## SUMMARY.

**119.** Sulphurous oxide is emitted from volcanoes, and is prepared by the action of copper on sulphuric acid. The gas has a pungent odor, is colorless, and may be easily condensed to a liquid by cold. It is very soluble in water, its solution being acid to litmus, and contains sulphurous acid, which forms a series of salts known as sulphites.

Sulphurous acid acts as a bleaching and disinfecting agent.

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## LABORATORY DIRECTIONS.

**120.** In inserting copper filings in a Florence flask, take care that they do not drop *through* the bottom; the best plan is to hold the flask in a horizontal position and slide them slowly in.

In heating sulphuric acid, be very careful to use every precaution to prevent the cracking of the flask; for instance, never allow the flame to play directly on the glass; always place a piece of wire gauze between the bottle and the flame; keep the flame rather small. Never hold the hands where there is any danger, in event of a breakage, of the hot acid running on them. Should, however, such a misfortune, by any accident, happen, *immediately* place the burned part under a continuous stream of cold water for at least 10 or 15 minutes, and *then* have the hand dressed by a physician.

To make a freezing mixture, pound together in a mortar 2 parts of ice and 1 part of salt.

### SULPHURIC OXIDE.

*Sulphuric oxide, sometimes called sulphur trioxide. Formula $SO_3$. Molecular weight 79.86. Density 39.93. One liter of sulphuric oxide vapor weighs 3.58 grams (39.93 criths).*

**121. Preparation.**—Sulphurous oxide and oxygen combine to form sulphuric oxide when passed through a tube containing heated platinum.

The combination may be shown by passing oxygen from the tube *A*, Fig. 39, connected with an oxygen-generating flask,

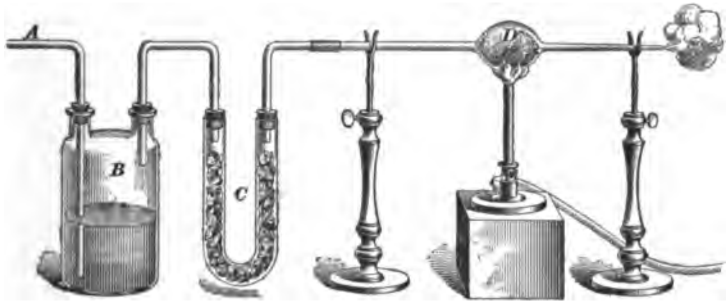


FIG. 39.

through a strong solution of sulphurous acid in bottle *B*, so that it may take up a quantity of $SO_2$; afterwards through a tube *C* containing pumice stone soaked with oil of vitriol, to remove the water; and then through a bulb *D* containing platinized asbestos (see "Laboratory Directions," Art. **134**). The mixture of the gases issuing into the air is quite invisible, but when the bulb *D* is gently heated combination takes place, and dense, white clouds are formed in the air, from the combination of the sulphuric oxide $SO_3$ produced with the atmospheric moisture. The oxide is also obtained by heating disulphuric acid; the vapor is collected in a cold and dry receiver.

$$\underset{\text{disulphuric acid}}{H_2S_2O_7} = \underset{\text{sulphuric acid}}{H_2SO_4} + \underset{\text{sulphuric oxide}}{SO_3}$$

**122. Properties.**—Sulphuric oxide thus obtained is a wax-like, white solid, which crystallizes in silky fibers

resembling asbestos. Its specific gravity is 1.9. It melts at 16° and boils at 46°. When purified by repeated distillation in hermetically sealed tubes, it changes into a colorless liquid. It is devoid of all acid properties, and may be handled with *dry* fingers without any injury. On passing sulphuric oxide through a red-hot tube, it is separated into oxygen and sulphurous oxide.

$$\underset{\text{sulphuric oxide}}{2SO_3} = \underset{\text{sulphurous oxide}}{2SO_2} + \underset{\text{oxygen}}{O_2}$$

Sulphuric oxide unites readily with water, with the evolution of great heat, producing sulphuric acid:

$$\underset{\text{sulphuric oxide}}{SO_3} + \underset{\text{water}}{H_2O} = \underset{\text{sulphuric acid}}{H_2SO_4}$$

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### SULPHURIC ACID.

*Formula $H_2SO_4$. Molecular weight 97.82. Specific gravity of liquid at 0°, 1.854, and at 12°, 1.842. Boiling point 338°.*

**123. History and Occurrence.**—The discovery of sulphuric acid dates back more than four centuries; it was first prepared by an alchemistically inclined monk, Basil Valentine, in the 15th century, who called it "*oleum sulphuris per campanum.*" Dr. Roebuck, an Englishman, proposed the present method of manufacture in 1770. The acid thus prepared is therefore often called *English sulphuric acid.*

Sulphuric acid occurs free, to a remarkable extent, in river and spring waters. Boussingault, a French chemist, estimates that the Rio Vinagre, in South America, carries daily to the sea more than 38,000 kilograms; and that the water of the Oak Orchard mineral spring, New York, contains, in each liter, about 2.5 grams.

Not only is sulphuric acid found in water, but the animal and mineral kingdom may also furnish us with it. It has been observed as a secretion of certain mollusks, the saliva of *Dolium galea Lk.* containing nearly 3½ per cent. of it; and

in the sulphates of iron, calcium, barium, and strontium, forming the minerals melanterite, gypsum, barite, and celestite, sulphuric acid is well represented.

**124. Importance of Sulphuric Acid.**—There is no other substance, with the single exception of water, that is of so great importance to the chemist, be he manufacturing or analyzing, as sulphuric acid. The frequency of its application to various purposes in the preceding experiments will have given the student some idea of its usefulness, and will already have made him somewhat familiar with its appearance, properties, etc.

**125. Preparation.**—Sulphuric acid, being manufactured on an immense scale in this country, as well as in England, is never prepared in the laboratory for actual use, but always bought.

A detailed description of the present process of manufacture will be very easily understood after a consideration of the principles of the chemical changes on which it depends.

Sulphurous oxide is produced by burning sulphur in the air, thus:

$$\underset{\text{sulphur}}{S_2} + \underset{\text{oxygen}}{2O_2} = \underset{\text{sulphurous oxide}}{2SO_2}$$

Sulphurous oxide and nitric acid in the presence of water produce sulphuric acid and nitrogen dioxide, according to the equation:

$$\underset{\text{sulphurous oxide}}{3SO_2} + \underset{\text{nitric acid}}{2HNO_3} + \underset{\text{water}}{2H_2O} = \underset{\text{sulphuric acid}}{3H_2SO_4} + \underset{\text{nitrogen dioxide}}{N_2O_2}$$

But nitrogen dioxide (sometimes also, but wrongly, called nitric oxide) in contact with air changes into nitrogen peroxide or nitrogen tetroxide:

$$\underset{\text{nitrogen dioxide}}{N_2O_2} + \underset{\text{oxygen}}{O_2} = \underset{\text{nitrogen tetroxide}}{N_2O_4}$$

which again, in the presence of water, serves to convert a further quantity of $SO_2$ into $H_2SO_4$, thus:

$$2SO_2 + N_2O_4 + 2H_2O = 2H_2SO_4 + N_2O_2$$

Nitrogen dioxide is in this way regenerated, and serves to convert still more $SO_2$ into $H_2SO_4$, if the requisite quantities of steam be supplied, the last two equations being repeated.

Should the supply of steam be deficient, nitrosyl sulphate is found deposited in crystals in the sulphuric-acid chambers, which is formed according to the following equation:

$$\underset{\substack{\text{sulphurous}\\ \text{oxide}}}{4SO_2} + \underset{\substack{\text{nitrogen}\\ \text{tetroxide}}}{2N_2O_4} + \underset{\text{oxygen}}{O_2} + \underset{\text{water}}{2H_2O} = \underset{\substack{\text{nitrosyl}\\ \text{sulphate}}}{4SO_2OHONO}$$

In the presence of a further quantity of $SO_2$ and $H_2O$, the nitrosyl sulphate is decomposed into sulphuric acid and nitrogen dioxide, thus:

$$2SO_2OHONO + SO_2 + 2H_2O = 3H_2SO_4 + N_2O_3$$

In fact, it is generally believed that these last two equations represent the reactions that take place in the acid chambers more truly than those quoted previously.

It is, however, seen from all these equations that, by employing $N_2O_3$ to absorb oxygen from the air and to convey it to the $SO_2$, theoretically an unlimited quantity of sulphur may be converted into sulphuric acid by a given quantity of $N_2O_3$ with a sufficient supply of air and steam.

The actual reactions involved in this process have received much attention, and full discussion of the probabilities may be studied in any of the numerous works on sulphuric-acid manufacture.

To illustrate the chemical principles of the manufacture of sulphuric acid upon the lecturer's table, the apparatus shown in Fig. 40 is usually employed.

EXPERIMENT 54.—A large Florence flask $A$, Fig. 40, is fitted with a cork, through which are passed a tube $a$ connected with a flask $D$ containing copper and strong sulphuric acid for evolving $SO_2$; a tube $b$ connected with a flask $B$ containing copper and diluted nitric acid

(specific gravity 1.2) for supplying nitrogen dioxide; a tube *c* proceeding from a small flask *E* containing water.

On heating the flask containing nitric acid and copper, the nitrogen dioxide passes into the Florence flask *A* and combines with the oxygen of the air, filling the flask *A* with a red mixture of nitrogen tetroxide and nitrous oxide. Sulphurous oxide is then evolved by heating the

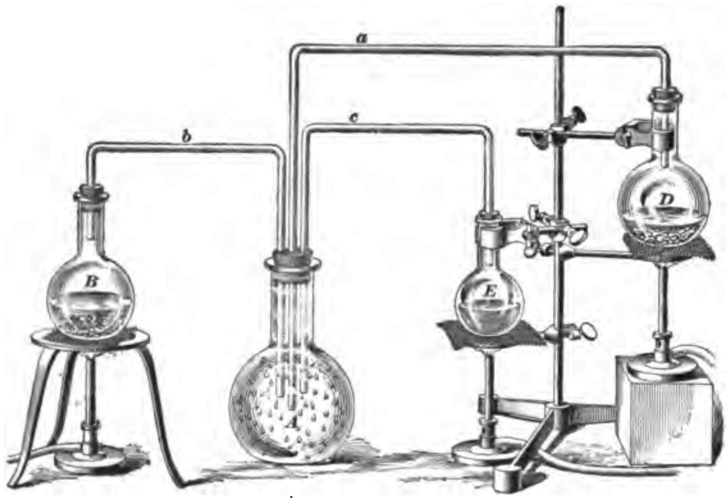



FIG. 40.

flask *D*; the sulphurous oxide will soon decolorize the red gas, the contents of the globe becoming colorless and a crystalline compound forming abundantly on the sides; the flask *D* may then be removed. Steam is next sent into the flask *A* from flask *E* by heating the water therein; the steam decomposes the crystals, and sulphuric acid gathers at the bottom of flask *A*.

If the experiment is repeated, and the steam and sulphurous acid admitted to flask *A* simultaneously, no crystalline compound will be formed, the sulphurous oxide being at once converted into sulphuric acid.

The process employed for the manufacture of sulphuric acid on a large scale will now be readily understood.

Sulphurous oxide is produced by burning sulphur, or, better, roasting sulphur ore (mostly pyrites), in a suitable furnace by which a mixture of air and sulphurous oxides is obtained. The reaction between the various bodies then occurs in large chambers made of timber framing and lined

with sheet lead, the joints being made air-tight by soldering the edges together with the oxyhydrogen blowpipe. Fig. 41 shows the general arrangement of a modern English sulphuric-acid works; *a*, *a* are two of a series of pyrite burners

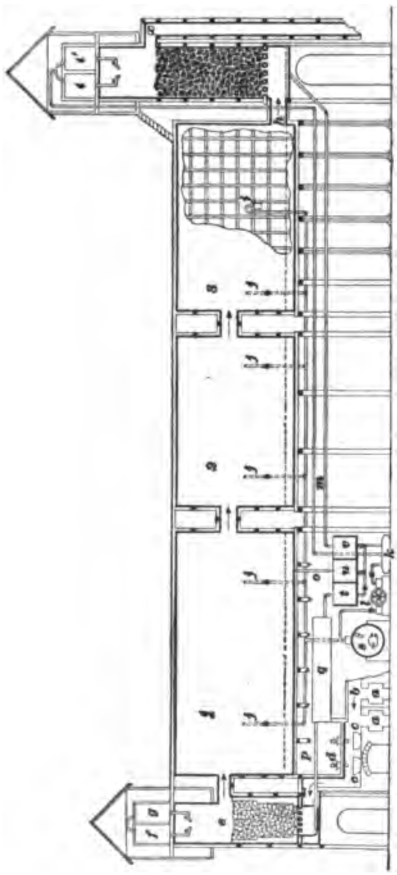


Fig. 41.

generating $SO_2$, which, passing along the flue *b*, heats the cast-iron troughs *c*, *c*, which are supplied with nitrate of soda and sulphuric acid through the funnels *d* for the production of nitric acid fumes, which, together with $SO_2$, proceed onwards to the *Glover* tower *e*. This tower consists of a framework of timber supporting a column of thick sheet lead, and lined with a wall of refractory bricks built without mortar and diminishing in thickness towards the top. The remaining space is filled either with large flints or with reticulated or "pigeonholed" brickwork, through the interspaces of which the gases pass upwards, meeting on their way sulphuric acid trickling downwards from the tanks *f* and *g* on the tower top, and so reach the first leaden chamber *1*, which consists, as has been already explained, of a timber framework lined with lead and supported on cast-iron pillars. Into this chamber steam from the boiler *s* is introduced by the jets *j*, *j* set in the side of the chamber. Here the

characteristic sulphuric-acid reaction occurs, and the acid collects on the bottom of the chamber, which, for this purpose, has been given the shape of a huge saucer. In this first chamber most of the $SO_2$ is converted into $H_2SO_4$, and the remaining gases, in which oxides of nitrogen begin to predominate, pass to a second chamber *2*, where they again meet with steam, and where a further precipitation of sulphuric acid takes place, leaving the remaining gases, still richer in nitrogen compounds and poorer in sulphurous oxide and acid, to pass into the next chamber *3*, where *nearly* the whole of the $SO_2$ is converted into liquid $H_2SO_4$. The remaining gases, which, theoretically, should now only consist of residual nitrogen, a necessary excess of oxygen, oxides of nitrogen, and a trace of sulphurous acid, pass from this chamber by the flue *h* to the *Gay-Lussac*, or *absorbing*, tower, which consists of a timber framework lined with lead, inside of which a wall built of bricks without mortar runs up. The inside space of this tower is filled with hard coke, down which sulphuric acid (specific gravity 1.75) trickles from the cisterns *i*, *i'*. This acid meets and absorbs the nitrogen oxides from the escaping gases, leaving only the excess of air, the atmospheric nitrogen corresponding to the oxygen taken up in the reactions, and a minute trace of $SO_2$. These pass from the tower by the exit flue *x* to the chimney of the works, which produces the draft for the arrangement, their escape being regulated by a damper not shown in the figure. The number of chambers in a series varies from two to six in different works; their shape and size also vary within certain limits, the average size being 100 ft. × 20 ft. × 20 ft.

It now only remains to explain the workings of the towers. Sulphuric acid of a specific gravity of 1.75 is run from the cistern containing *strong acid* (*t* in the figure) into a closed cast-iron vessel *k*, technically known as an "egg." When the egg is filled, the valve communicating with the cistern is closed, and a valve is opened that connects the egg with a powerful air-pumping engine *l*, which, working up to a pressure of 60 pounds per square inch, forces the acid out of the egg, up the pipe *m*, into the cisterns *i*, *i'*, at the top of the

absorbing tower, whence it slowly trickles down through the coke, taking up the nitrous compounds, and running by way of the pipe below *m* to the nitrous-acid cistern marked *v*, whence, as required, it is run into the egg and forced or blown through a pipe similar to *m*, but not shown in the figure, to the cistern *f* on top of the Glover tower. The acid made in the chambers, which possesses a specific gravity of 1.60, is drawn from time to time by pipe *o* into the so called *chamber-acid* cistern marked *u* in the figure, from which it is blown into cistern *g* on the Glover tower. The run of nitrous acid from cistern *f* and of chamber acid from cistern *g* is so adjusted that, after trickling down the hot flints or bricks and meeting the hot mixture of gases on its way through the tower, the acid runs off by the pipe *p*. Deprived of its nitrous compounds, which, as we have seen, enter the chambers, and concentrated by the heat to a specific gravity of from 1.73 to 1.75, it passes through a coil of lead piping immersed in cold water (in the cooler), which cools it from about 72° to about 16°, thence to the "strong-acid" cistern *t*, whence it is taken for use as required.

It will be easily understood that the two towers effect an economy by considerably reducing the necessary amount of the most costly raw material, nitrate of soda, and that the Glover tower saves a considerable amount of coal by concentrating the acid and thus supplying steam to the chambers by utilizing the heat from the pyrite burners. Moreover, by cooling, and, consequently, contracting the volume of the gases, it makes the existing chamber capacity so much more effective.

The acid is further concentrated by evaporation in either glass or platinum vessels, until a specific gravity of 1.842 is reached, when it is brought into commerce as "concentrated English sulphuric acid."

**126. Properties.**—Common concentrated sulphuric acid is a dense, colorless acid of oily consistency, having a specific gravity of 1.842, and contains about 1.5 per cent. of water. It boils at about 338°, and solidifies when cooled to a low

temperature, the crystals thus formed having the composition $H_2SO_4$, and a specific gravity of 1.837; it melts again at 10.8°. Sulphuric acid may be distilled, but undergoes then a partial decomposition, the product containing but 98.7 per cent. of acid. Sulphuric acid possesses an exceedingly strong attraction for water, combining with it with the evolution of great heat. It attracts moisture from the air, and from its avidity to absorb water is largely used in the laboratory as a drying agent for gases, the gas to be dried being caused to bubble through the acid. It also attacks most organic substances, removing the water from them, and thus completely charring or blackening them. When bodies have an excess of carbon that element is liberated.

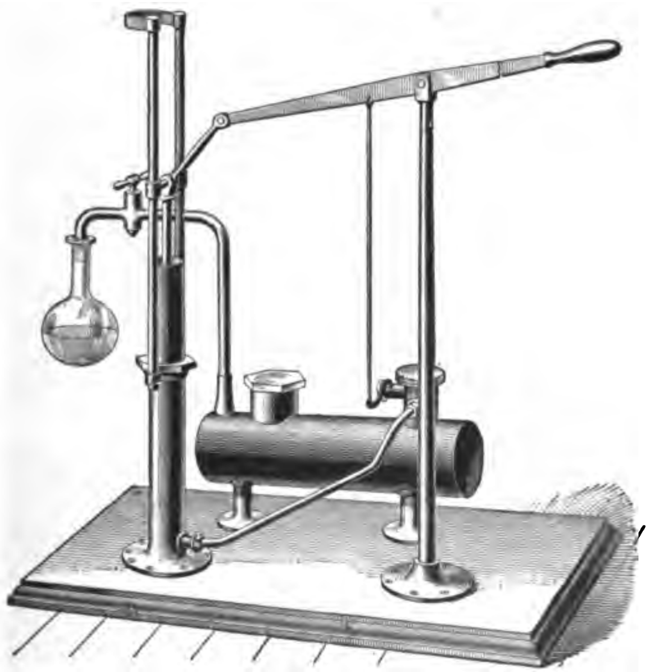


FIG. 42.

EXPERIMENT 55.—Prepare a saturated solution of sugar and water; pour about 5 cubic centimeters of it into a beaker, and add all at once

10 cubic centimeters of sulphuric acid; the mixture suddenly froths up with great heat, a blackened and charred mass remaining.

This property of sulphuric acid is turned into account in the manufacture of shoe-blacking, in which treacle and sulphuric acid are employed.

Even when largely diluted, sulphuric acid corrodes textile fabrics very rapidly, and, though the acid is too diluted to appear to injure them at first, it will be found that the water evaporates by degrees, leaving the acid in a more concentrated state, and the fiber of the fabric is then perfectly rotten.

The attraction of sulphuric acid for water is made use of for the production of ice in an ice-producing apparatus invented by E. Carré, of Paris. Fig. 42 represents this ice-producing machine. The water to be frozen is placed in the flask on the left, which is connected by a tube with a horizontal vessel containing sulphuric acid; this vessel may be exhausted by the air pump, the sulphuric acid being constantly agitated by means of a stirrer. The water is cooled by its own evaporation under the diminished pressure, and, as the vapor is at once removed by the sulphuric acid, it soon congeals. A pint of water may be frozen in 15 seconds with this apparatus.

Sulphuric acid, being a dibasic acid, forms two well marked series of salts, the one of which is normal; while the other, still containing half the hydrogen, is acid.

At a white heat, sulphuric acid is decomposed into water, sulphurous oxide, and oxygen.

**127. Pyrosulphuric, Disulphuric, or Nordhausen Sulphuric, Acid** $H_2S_2O_7$.—This is another kind of sulphuric acid met with in commerce. It may be regarded as a compound of a molecule of ordinary sulphuric acid with a molecule of sulphuric oxide:

$$H_2SO_4 + SO_3 = H_2S_2O_7$$

It is prepared by the distillation of partially dried ferrous sulphate in earthen retorts; it is named after a town in the province of Saxony, where it is manufactured on a large scale, and is used largely for dissolving indigo, with which the

celebrated Saxony blues are made. It is a heavy, oily liquid of specific gravity 1.9. It is usually more or less dark-colored, and hisses like a hot iron when dropped into water; it fumes strongly when exposed to air, and is, consequently, very often called "*fuming sulphuric acid.*"

Disulphuric acid is now manufactured on a large scale by conducting sulphuric oxide, made by passing sulphurous oxide and oxygen over platinized asbestos at a high temperature, through ordinary sulphuric acid. It is sometimes called *solid* sulphuric acid, because it solidifies when cooled, forming crystals which melt at 35°.

**128. Tests.**—The test for free sulphuric acid is the characteristic charring it causes. A natural water containing sulphuric acid, if used to moisten paper, will char it completely on drying at 100°. In combination in a soluble form, sulphuric acid and sulphates give a dense white precipitate with solution of barium chloride, insoluble in acids. If the sulphate is insoluble in water, it may be recognized by fusing it with sodium carbonate, thus converting it into sodium sulphate, which is soluble in water, and may be tested as above. Or, which is sometimes preferable, the suspected sulphate may be heated for some time with pulverized charcoal; it will thus be reduced to a sulphide, which, on treatment with a drop of acid, will evolve the well known smell of hydrogen sulphide.

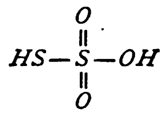
**129. Uses.**—Sulphuric acid is not only one of the most important substances used in the laboratory, but it is of equal importance in the manufacture of chemicals. It is used in the production of nitric, phosphoric, hydrochloric, citric, and tartaric acids, in the manufacture of soda, of phosphorus, and of alum; it is employed to a very great extent in dyeing, bleaching, and calico printing, in the preparation of fertilizers, and in the refining of petroleum.

It is estimated that England alone produces about 100,000 tons of sulphuric acid annually for home consumption, and at least an equal amount for export.

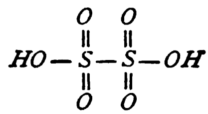
**130.** Besides the acids previously mentioned, which, with the exception of pyrosulphuric acid, contain only 1 atom of sulphur, there is a series of others, which contain more than 1 atom (with different valences) of sulphur.

This group of acids is commonly known as the *thionic series*, derived from a Greek word meaning "sulphur," and includes the following substances:

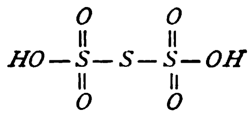
Thiosulphuric acid $H_2S_2O_3$



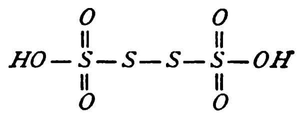
Dithionic acid $H_2S_2O_6$



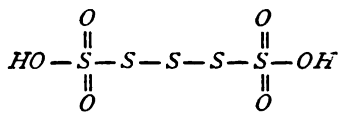
Trithionic acid $H_2S_3O_6$



Tetrathionic acid $H_2S_4O_6$



Pentathionic acid $H_2S_5O_6$



**131. Thiosulphuric Acid.**—Thiosulphates are prepared either by adding sulphur to a sulphite or by partial oxidation of a sulphide. By the first method:

$$\underset{\text{sodium sulphite}}{2Na_2SO_3} + \underset{\text{sulphur}}{S_2} = \underset{\text{sodium thiosulphate}}{2Na_2S_2O_3}$$

Sodium thiosulphate, commonly, but erroneously, called sodium hyposulphite, is extensively manufactured for use in photography, serving to fix prints by dissolving the unaltered portion of the sensitive film of silver chloride, bromide, or iodide. It is also used in the chlorine bleaching process.

### SULPHUR AND CHLORINE.

**132.** Three compounds of sulphur and chlorine are known:

$Cl_2S_2$, *sulphur monochloride*
$Cl_2S$, *sulphur dichloride*
$Cl_4S$, *sulphur tetrachloride*

They are formed by the direct union of their constituents, the first being formed when the sulphur is present in excess, the last when the chlorine is most abundant. Sulphur monochloride, or, as it is also called, *disulphide of chlorine*, is an active reddish-yellow liquid, specific gravity 1.687, possessing a peculiar, penetrating, disagreeable odor, fuming strongly in the air, and boiling at 136°.

*Sulphur dichloride* $Cl_2S$ is prepared by passing chlorine to saturation into sulphur monochloride cooled by a mixture of ice and salt, and expelling the excess of chlorine by a stream of carbon dioxide. The compound thus obtained is a dark-red liquid, containing 30.5 per cent. of sulphur and 69.5 per cent. of chlorine, and agreeing nearly with the formula $SCl_2$, which requires 31.07 per cent. of sulphur and 68.93 per cent. of chlorine.

*Sulphur tetrachloride* $Cl_4S$ is prepared by saturating chlorine disulphide with chlorine at a temperature of −20°. The product contains 81.59 per cent. of chlorine and 18.41 per cent. of sulphur, while the percentage calculated from the formula $Cl_4S$ is 81.61 per cent. and 18.39 per cent. The tetrachloride exists not only in the free state, but also in combination with certain metallic chlorides, as $SnCl_4(Cl_4S)_2$ with stannic chloride, and $SbCl_5(Cl_4S)_3$ with antimonic chloride.

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### SUMMARY.

**133.** Sulphuric oxide is a non-acid body produced by the union of sulphurous-acid gas with oxygen; the two combine when passed through platinized asbestos. It has no action on litmus, but has a great affinity for water, with which it produces sulphuric acid.

Sulphuric acid is a compound of great importance; it is formed by the oxidation of sulphurous acid, either by the atmosphere or some oxidizing agent such as nitric acid, etc.

Sulphuric acid is manufactured by the reactions occurring between sulphur dioxide, oxygen, nitric acid, and steam. The dilute acid is concentrated by evaporation. Nordhausen sulphuric acid is prepared by heating ferrous sulphate. Sulphuric acid is a colorless, odorless liquid, having a great attraction for water. Being a dibasic acid, it forms two series of salts called sulphates.

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### LABORATORY DIRECTIONS.

**134.** Platinized asbestos, mentioned in Art. **121,** may be obtained by wetting some asbestos with a solution of platinic chloride and heating this to redness, whereby the platinum is reduced to the metallic state, thus covering the asbestos with a thin film of platinum.

Performing Experiment 54, it will be found that the cork of flask *A* (Fig. 40) is more or less corroded. It is, therefore, preferable to have the mouth of the flask ground and closed by a ground plate glass perforated with holes for the passage of the glass tubes. The perforations are readily made by placing the glass plate flat against the wall and piercing it with the point of a revolving rat-tail file dipped in turpentine; the file is then gradually worked through the hole until the latter is of the required size.

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## SELENIUM.

*Symbol Se. Atomic weight 78.58. Molecular weight 157.16. Density 78.58. Valence II, IV, VI. Specific gravity of solid 4.5. The weight of 1 liter of selenium vapor at 1,420° is 7.04 grams (78.58 criths).*

**135. History.**—Selenium, a name derived from the Greek word for "moon," is a rather rare element. It is very

closely allied to sulphur, so far as its natural history, physical character, and chemical relationship to other bodies are concerned. It is found sparingly in the free state, associated with sundry varieties of native sulphur, but more generally combined with certain metals, forming *selenides*, which are mostly found together with the sulphides. The iron pyrites of Fahlun, in Sweden, are especially remarkable for the presence of selenium, and are the source from which this element was first obtained. The Fahlun pyrites are largely employed in the manufacture of sulphuric acid, and in the lead chambers of certain sulphuric-acid works a reddish-brown deposit is found, which was analyzed by Berzelius in 1817, and found to contain a new element, which he named selenium.

**136. Preparation.**—Selenium is obtained from the sulphuric-acid residue, generally termed the *seleniferous deposit*, of the sulphuric-acid works, by boiling it with sulphuric acid diluted with an equal volume of water, and by adding nitric acid in small portions till the oxidation is complete, when no more red fumes will escape. The solution, containing selenious and selenic acids, is largely diluted with water, filtered from the undissolved matters, mixed with about one-fourth of its bulk of hydrochloric acid and somewhat concentrated by evaporation, when the hydrochloric acid reduces the selenic to selenious acid, thus:

$$H_2SeO_4 + 2HCl = H_2SeO_3 + H_2O + Cl_2$$

A current of sulphurous-oxide gas is now passed through the solution, when the selenium is precipitated in fine, red flakes, which collect into a dense, black mass when the liquid is gently heated.

$$H_2SeO_3 + H_2O + 2SO_2 = 2H_2SO_4 + Se$$

The proportion of selenium in the seleniferous deposits varies to a certain extent. The writer, while working in one of the largest sulphuric-acid works, has repeatedly obtained from 1.5 per cent. to 1.97 per cent. of selenium by this

process; but a number of authorities on chemistry have obtained, especially from English works, as high as 3 per cent.

**137. Properties.**—Like sulphur, selenium is capable of existing in various allotropic modifications: ($\alpha$)* Selenium is a dark, grayish-black, crystalline solid, of specific gravity 4.8, and is insoluble in carbon disulphide. It is a conductor of electricity and possesses a metallic luster. ($\beta$)† Selenium is of a dark, reddish-brown color, having a specific gravity of 4.5, and is soluble in carbon disulphide, from which it crystallizes in prismatic crystals. This variety is the most stable form of selenium, the one it has when native. A third, amorphous variety is also existing. This amorphous form possesses a specific gravity of 4.26, and exists in two distinct forms: the one electropositive and insoluble in carbon disulphide, the other electronegative and soluble in carbon disulphide. It fuses a little above 100°, and, if suddenly cooled, becomes vitreous selenium. When heated to 270° and then suddenly cooled to about 180°, keeping this temperature constant for some time, the amorphous variety is converted into the crystalline ($\alpha$) selenium. On raising the temperature to 150°, the ($\beta$) variety passes into ($\alpha$) selenium with a distinct evolution of heat. The ($\beta$) variety of selenium melts at 217°, the liquid boiling at about 700°.

In its chemical properties selenium very closely resembles sulphur, forming similar compounds with other elements. Selenium burns with a blue flame and gives off an offensive odor, resembling that of decaying horseradish. It unites directly with metals, forming *selenides*.

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## COMPOUNDS OF SELENIUM.

**138. Selenium Dioxide** $SeO_2$.—This compound corresponds to sulphurous oxide, and is the product of the combustion of selenium in oxygen. It is best obtained by

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* $\alpha$ = *alpha*, the Greek letter representing our *a*.
† $\beta$ = *beta*, the Greek letter representing our *b*.

dissolving selenium in boiling nitric acid and evaporating to dryness, when the selenium dioxide remains as a white solid, which sublimes in needle-like crystals when heated. When dissolved in boiling water, it yields crystalline *selenious acid* $SeO(OH)_2$.

**139. Selenic Acid** $H_2SeO_4$, or $SeO_2(OH)_2$.—Potassium selenate is formed when selenium is oxidized by fused niter, thus:

$$\underset{\text{(or potassium nitrate)}}{\underset{\text{niter}}{2KNO_3}} + \underset{\text{selenium}}{Se} = \underset{\text{selenate}}{\underset{\text{potassium}}{K_2SeO_4}} + \underset{\text{dioxide}}{\underset{\text{nitrogen}}{N_2O_2}}$$

By dissolving the potassium selenate in water, and adding lead nitrate, a precipitate of lead selenate $PbSeO_4$ is obtained, and, if this is suspended in water and decomposed by passing hydrogen sulphide through, lead will be removed as insoluble sulphide, and a solution of selenic acid will be obtained:

$$\underset{\text{selenate}}{\underset{\text{lead}}{PbSeO_4}} + \underset{\text{sulphide}}{\underset{\text{hydrogen}}{H_2S}} = \underset{\text{acid}}{\underset{\text{selenic}}{H_2SeO_4}} + \underset{\text{sulphide}}{\underset{\text{lead}}{PbS}}$$

This solution may be evaporated till it has a specific gravity of 2.6, and heated in a vacuum at 180° as long as any distils over; the residue will crystallize on cooling. The crystals (specific gravity 2.5) melt at 58° and are deliquescent.

**140. Hydroselenic Acid** $H_2Se$.—Hydrosélenic acid, sometimes called *selenieted hydrogen*, is the analogue of $H_2S$. It is, however, more offensive and poisonous than hydrogen sulphide, and acts in a similar way upon metallic solutions, precipitating the *selenides*.

**141.** There are two chlorides of selenium known; namely, the monochloride $Se_2Cl_2$, a brown, volatile liquid. and the tetrachloride $SeCl_4$, a white, crystalline solid.

**142.** Notwithstanding the resemblance between selenium and sulphur, sulphides of selenium are known, probably $SeS_2$ and $SeS_3$. The former is obtained as a yellow precipitate when hydrogen sulphide is passed into selenious acid.

## TELLURIUM.

*Symbol Te. Atomic weight 127. Valence II, IV, and VI. Density 127. Specific gravity of solid 6.25. One liter of tellurium vapor weighs at 1,390°, 11.37 grams (127 criths).*

**143. History and Occurrence.**—Tellurium was discovered by Klaproth in 1798, in a Transylvanian gold ore, who named it tellurium, from *tellus*, "the earth." It is a rarer element than selenium, and occurs native in Colorado and in Hungary. It also exists in combination with bismuth, lead, silver, and gold. *Foliated* or *graphic tellurium*, or *sylvanite*, is a black material containing the tellurides of silver and gold.

**144. Preparation.**—Tellurium is extracted from the foliated ore by a process similar to that for obtaining selenium. From bismuth telluride it is produced by strongly heating the ore with a mixture of potassium carbonate and charcoal, when potassium telluride is formed, which dissolves in water to a purple-red solution, from which tellurium is deposited on exposure to air:

$$\underset{\text{potassium telluride}}{2K_2Te} + \underset{\text{oxygen}}{O_2} + \underset{\text{water}}{2H_2O} = \underset{\text{potassium hydrate}}{4KOH} + \underset{\text{tellurium}}{Te_2}$$

The tellurium thus obtained is not altogether pure, nor has tellurium thus far been obtained free from other elements, although the nature of these is yet unknown.

**145. Properties.**—Tellurium is a white, brittle solid with a strong metallic luster and a specific gravity of 6.25. It conducts heat and electricity readily, and crystallizes in rhombohedrons. It melts at 500°, volatilizes at white heat, and can be distilled. Its vapor is greenish yellow, resembling that of chlorine. When heated in the air, it takes fire and burns with a blue flame tinged with green, evolving white fumes of tellurous oxide.

In all its physical properties, tellurium closely resembles a

metal, but, being so closely allied, chemically, to sulphur and selenium, it is justifiable to regard it as a non-metal and consider it with these elements.

Its binary compounds are known as *tellurides*.

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### SUMMARY.

**146.** The same gradation of properties that has been noticed in the halogen group may be noticed between the three elements, sulphur, selenium, and tellurium, a group of closely allied elements commonly known as the *sulphur group*.

As the atomic weight of its members increases, their chemical activity diminishes. The sum of the atomic weights of sulphur and tellurium ($31.98 + 128$) is slightly more than double that of selenium (78). All these three elements form compounds with hydrogen, which are similar in form to water $H_2O$, $H_2S$, $H_2Se$, and $H_2Te$, in which they are bivalent; and the last three form oxides in which their valence is IV and VI; as, $SO_2$ and $SO_3$; $SeO_2$ and $SeO_3$; $TeO_2$ and $TeO_3$, to each of which there is a corresponding acid.

# INORGANIC CHEMISTRY.

(PART 2.)

## NON-METALS OR METALLOIDS.

### NITROGEN.

*Symbol N. Atomic weight 14.01. Density 14.01. Valence III and V. Specific gravity .971. Molecular weight 28.02. One liter weighs 1.255 grams (14.01 criths).*

**1. History.**—Nitrogen was discovered by Rutherford in 1772, who showed that air, after it had been breathed by an animal and washed with lime water, contained a gas that would support neither respiration nor combustion. Scheele and Lavoisier soon afterwards found, independently of each other, that this substance constituted four-fifths of the air. Lavoisier gave it the name of *azote*, and Chaptal later proposed the name of *nitrogen*.

**2. Occurrence.**—Nitrogen exists in the free state in the atmosphere, and in combination with oxygen and metals in certain native nitrates, besides being an essential constituent of many vegetable and animal substances.

**3. Preparation.**—The easiest method of preparing nitrogen is by burning out of a given volume of air the

oxygen it contains, thus leaving the nitrogen. It may also be procured by purely chemical processes; as, for instance, by heating ammonium nitrite:

$$(NH_4)NO_2 = 2H_2O + N_2$$

EXPERIMENT 1.—Nitrogen may be obtained from air by burning out the oxygen by means of phosphorus or copper. A small piece of phosphorus carefully dried, is placed in a light receptacle floated upon the surface of water by means of a piece of cork. The phosphorus is lighted and then quickly covered with a good sized bell (glass), as shown in Fig. 1. Dense white fumes are formed by the combustion, which fill the jar; the oxygen is gradually consumed, and the water rises in the bell jar to take its place. After a short time these fumes disappear, and the nitrogen is left comparatively pure.

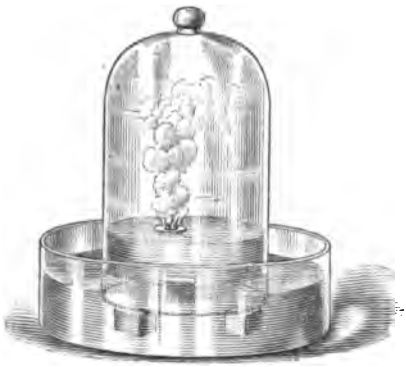

FIG. 1.

The oxygen may also be removed by the action of metallic copper. If an iron tube is filled with copper turnings, and made red hot in a furnace, the copper immediately combines with the oxygen of any air that may be passed through, leaving the nitrogen; thus,

$$2Cu + O_2 = 2CuO$$

Iron likewise removes the oxygen from air, especially if the iron is caused to oxidize more readily by the addition of some ammonium chloride.

There are various other methods of preparing nitrogen, all of which are interesting from a theoretical point of view.

For instance, the gas is evolved by passing chlorine into an excess of ammonia. The hydrogen and chlorine unite, and nitrogen is liberated.

$$\underset{\text{ammonia}}{2NH_3} + \underset{\text{chlorine}}{3Cl_2} = \underset{\text{hydrochloric acid}}{6HCl} + \underset{\text{nitrogen}}{N_2}$$

A secondary reaction goes on between the acid formed and the excess of ammonia; thus,

$$\underset{\text{ammonia}}{6NH_3} + \underset{\text{hydrochloric acid}}{6HCl} = \underset{\text{ammonium chloride}}{6NH_4Cl}$$

These two reactions may be expressed through one equation; thus,

$$\underset{\text{chlorine}}{3Cl_2} + \underset{\text{ammonia}}{8NH_3} = \underset{\text{ammonium chloride}}{6NH_4Cl} + \underset{\text{nitrogen}}{N_2}$$

EXPERIMENT 2.—Prepare a flask $A$ for the evolution of chlorine; arrange a second flask $B$ as a wash bottle, with the delivery tube $C$ very wide, and place in it about 60 grams of the strongest solution of

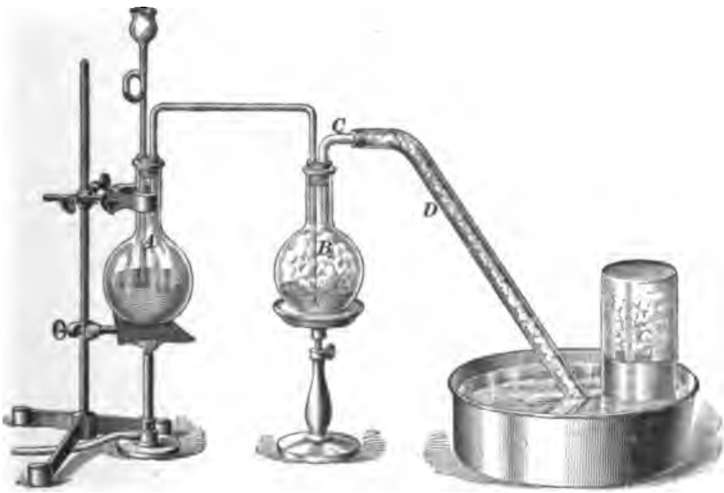


FIG. 2.

ammonia; connect to the chlorine flask, and to the delivery tube of the wash bottle attach a piece of glass tubing $D$, of larger diameter, leading into the pneumatic trough. The general arrangement of the apparatus is shown in Fig. 2. Heat the chlorine mixture; as each bubble of chlorine passes into the ammonia solution, dense white fumes of ammonia chloride are produced. A wide leading tube is used, because

**a narrow one might be easily choked by the accumulation of this salt. Considerable heat is evolved, and the action is so intense that flashes of light accompany the combination of chlorine and hydrogen.**

While performing this experiment, the student should bear in mind that it is a rather dangerous one; and strict attention should be paid to the laboratory directions (Art. **10**), or else the experiment is very likely to come to a sudden and disastrous end for the student.

**4. Properties.**—Nitrogen is an odorless, colorless, and tasteless gas; it is somewhat lighter than air, having a specific gravity of .971. It extinguishes burning bodies and is not combustible itself. Water dissolves only $\frac{1}{50}$ of its volume of nitrogen at 0°. Animals are quickly suffocated in an atmosphere of pure nitrogen, though the gas by itself does not exert any poisonous influence upon the animal economy.

It has been liquefied at temperatures below −146°, and under a pressure of 1 atmosphere this liquid boils at −190°.

Nitrogen is a remarkably inert body, combining directly with only a very small number of elements, among which may be mentioned magnesium, silicon, boron, and titanium. Strange as it may appear, nitrogen in a free state is very inactive, but its compounds are among the most energetic known. The corrosive nitric acid, the pungent ammonia, the explosive nitroglycerin, and even such an active poison as prussic acid, as well as numerous alkaloids, all contain more or less nitrogen.

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## THE ATMOSPHERE.

*A gaseous mixture. Density 14.43. Specific gravity 1.00.*

**5. Occurrence.**—The aerial envelope surrounding the earth is of vital importance to all beings that live and breathe in it, and is called *atmosphere*. Its existence is demonstrated whenever it is set in motion, as then we have *winds;* and these, when sufficiently violent, produce well known and striking physical effects.

**6. Properties.**—Careful experiments have shown that, among other properties of matter, the atmosphere possesses *weight*. Regnault has shown that 1 liter of air weighs 1.29318 grams at 0° under a pressure of 760 millimeters. It is, therefore, 14.43 times heavier than hydrogen. It has been chosen as the standard of specific gravity for gases. Torricelli showed, in 1643, that the pressure of the air upon the earth's surface would sustain a column of mercury about 76 centimeters in height; and, as a column of mercury of this height, with an area of 1 square centimeter, weighs 1,033 grams, it follows that this number represents the atmospheric pressure upon every square centimeter of the earth's surface.

**7. Composition.**—The atmosphere consists chiefly of a mixture of nitrogen with one-fifth of its volume of oxygen. In addition to these two elements, there are also present varying quantities of aqueous vapor, carbon dioxide, ammonia, nitric acid, and traces of other bodies. The average composition of the atmosphere is approximately shown in Table 1.

---

TABLE 1.

| | |
|---|---|
| Oxygen | 20.61 parts. |
| Nitrogen | 77.95 parts. |
| Carbon dioxide | .04 parts. |
| Aqueous vapor | 1.40 parts, |
| Nitric acid<br>Ammonia<br>Methane<br>Hydrogen sulphide<br>Sulphur dioxide | Traces, according to the location—whether city, village, seashore, etc. |

Although the proportion of oxygen in the air at a given place may be diminished, and that of carbon dioxide increased by processes of oxidation, such as respiration and combustion, taking place there, the operations of wind and of diffusion so rapidly mix the altered air with the greater general mass of the atmosphere that the variations in the composition of air in different places are very slight.

In a strictly accurate determination of the proportion of


FIG. 8.

oxygen to nitrogen in the atmosphere, it is naturally necessary to guard against any error arising from the presence of aqueous vapors, carbon dioxide, ammonia, etc. With this end in view Dumas and Boussingault, to whom we are originally indebted for our exact knowledge of the composition of the atmosphere, caused it to pass through a series of **U** tubes (see *A*, Fig. 3) containing potash, in order to remove the carbon dioxide ; then through a second series of **U** tubes *B* containing sulphuric acid, to absorb the ammonia and water ; the air thus purified was then passed through a glass tube *C* filled with copper heated to redness in a charcoal furnace, which removed the whole of the oxygen, and allowed the pure nitrogen to pass into the globe *D*.

Both the tube *C* (containing the copper) and the globe *D* were carefully exhausted of air by means of an air pump, and accurately weighed before the experiment; on connecting the globe and the tube with the purifying apparatus and slowly opening the stop-cocks *E* and $E_1$, the pressure of the external air caused the air to flow through the series of tubes, including *C*, where the atmosphere was decomposed, and the remaining nitrogen passed into the globe *D*. When a considerable quantity of air had passed in, the stop-cocks were again closed, and, after cooling, the weight of the globe was again accurately determined. The difference between this weight and that of the exhausted globe, before the experiment, gave the weight of the nitrogen that had entered the globe; but this did not represent the whole of the nitrogen contained in the analyzed air, for the tube containing the copper had, of course, remained full of nitrogen at the close of the experiment. This tube having been weighed was attached to the air pump, the nitrogen exhausted from it, and the tube weighed again; the difference between the two weighings furnished the weight of the nitrogen remaining in the tube, and was added to the weight of that received in the globe. The oxygen was represented by the increase of the weight of the exhausted tube containing the copper, which was partially converted into $CuO$ by combining with the oxygen of the air passed through it.

**8. Air a Mixture.**—The fact that air is a mixture and not a chemical compound may be proved in numerous ways. In the first place, the oxygen and nitrogen are not present in any simple multiple of their atomic weights, which, as we have seen, is necessary in all chemical compounds. Air also differs remarkably from all those compounds of these two elements with which chemistry is acquainted. If, furthermore, a mixture is made of nitrogen and oxygen in the proportion in which they exist in air, it will be found that no alteration of volume takes place, and that there is no increase of temperature; the mixture simply exhibits all the properties of ordinary atmospheric air.

The most conclusive evidence that these gases are mixed and *not* combined, is that they may be separated by the action of water as a solvent. Oxygen is much more soluble than nitrogen, and if water, which has been previously freed from gases by boiling, is shaken up with air, and then again boiled, the expelled gas is found on analysis to be much richer in oxygen than was the air, the oxygen amounting to about 34 per cent. of the dissolved gas.

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## SUMMARY.

**9.** Nitrogen exists in a free state in the atmosphere, and is also found in nitrates and numerous organic bodies. It is prepared by the removal of oxygen from the air by the action of either phosphorus or copper, or by the decomposition of bodies containing nitrogen, as ammonium nitrate and ammonia.

Nitrogen is a colorless, tasteless, and odorless gas, neither inflammable nor a supporter of combustion. It is neutral to litmus paper; it may be liquefied; by great heat it may be made to combine with oxygen, forming acid compounds.

The atmosphere is a mixture, and not a compound, of oxygen and nitrogen, in which small quantities of other compounds are also present.

#### LABORATORY DIRECTIONS.

**10.** In preparing nitrogen by the action of chlorine and ammonia, as described in Experiment 2, strict attention must be paid to the direction *always to have an excess of ammonia.* Should the student venture to perform this experiment, he must take great care to procure the strongest solution of ammonia (*Sp. Gr. .88*) from some chemical-supply company. Under no circumstances should the dilute solution (aqua ammonia), which is usually employed in the laboratory for analytical purposes only, be used. These precautions are necessary, because with an excess of chlorine a most violently explosive compound of nitrogen and chlorine is formed. The wide leading tube is also essential.

## NITROGEN AND HYDROGEN.

#### HYDROGEN NITRIDE, OR AMMONIA.

*Formula* $NH_3$. *Density 8.5. Molecular weight 17.01. One liter of hydrogen nitride weighs .762 gram (8.5 criths).*

**11. History.**—Ammonia has been known for many centuries. The alchemist Raymond Lully mentions it in his manuscript in the 13th century, and Basil Valentine used ammonia experimentally in the 15th century. Priestley, in 1774, first obtained it as a gas, while in 1777 Scheele analyzed it and showed it to contain nitrogen. The name *ammonia* was given by Bergman in 1782, derived from that of its chloride, then known as *sal ammoniac.*

**12. Occurrence.**—Ammonia exists in the free state in small quantities in the air and in rain water. It is generally a post-mortem product, as dead animal and vegetable matter yields it in putrefaction. The urine and excrement of

animals contain refuse nitrogenous matter, which, on being exposed to the air, becomes changed into ammonia, and in this way causes these substances to be such valuable manures, as plants are incapable of assimilating nitrogen in a free state, but are able to do so when that element is presented to them as ammonia.

The compounds of ammonia are found in beds of guano (the excrement of sea fowl) on certain ocean islands, etc. The most important of these compounds, *sal ammoniac*, was first obtained from Egypt. The name ammonia is said to be derived from that of Jupiter Ammon, owing to the circumstance that near a temple dedicated to this god the Arabs extracted one of the compounds of ammonia from the dung of camels. Quills, horn, hair, etc. heated in a closed vessel evolve a number of gases, among which ammonia is always present. Coal (fossilized plants) contains about 2 per cent. of nitrogen, and in its destructive distillation for the manufacture of gas, liquor ammoniæ, largely used in medicine and the arts, is always obtained. Considerable quantities of ammonia are now being recovered from the products of combustion obtained from blast furnaces, in which it originates from the distillation of coal.

**13. Preparation.**—Ammonia cannot be produced by the direct union of its constituents, but may be prepared from any of the ammoniacal salts by heating with a stronger base, such as lime or soda. Of these, lime is mostly chosen on account of its cheapness. If, for instance, ammonium chloride and lime are heated together, the following reaction occurs:

$$\underset{\text{ammonium chloride}}{2NH_4Cl} + \underset{\text{quick-lime}}{CaO} = \underset{\text{calcium chloride}}{CaCl_2} + \underset{\text{water}}{H_2O} + \underset{\text{ammonia}}{2NH_3}$$

EXPERIMENT 3.—Fit up a Florence flask with a cork and single-delivery tube, but at the same time be very careful that the flask, cork, and glass tubing are perfectly dry. Dry separately some powdered lime and ammonium chloride (sal ammoniac); the lime may be dried by simply heating it in a sand bath. To dry the ammonium chloride,

place it in an evaporating basin, and heat gently either in the sand bath or on a piece of wire gauze over the Bunsen flame turned down very low, as the heat must not be sufficient to cause any fumes to be evolved. After these two substances are thoroughly dried and again cooled, take about 7 grams (12 cubic centimeters of your measuring glass) of the ammonium chloride and about 14 grams (24 cubic centimeters) of the lime. Mix thoroughly in a mortar the ammonium chloride with about two-thirds of the lime; pour the mixture into the Florence flask, and then add the remaining lime in a layer over the top. Fix the flask in the retort stand, with a piece of wire gauze underneath; arrange the leading tube upright, so that the gas may be collected by upward displacement; invert a dry glass bottle over the leading tube, the end of which must reach right up to the top. Fig 4 shows the whole arrangement. Apply a gentle heat to the flask; the gas is evolved readily. To ascertain when the jar is full, hold a piece of reddened litmus paper outside the bottle just above the mouth; it will turn blue if the bottle is filled. Draw the tube out of the bottle, lift it from the ring, and quickly place on a cover.

FIG. 4.

EXPERIMENT 4.—Then attach, by means of a piece of rubber tubing, another piece of glass tubing, and place the end of it in a little distilled water in a beaker or tumbler; observe that the evolved ammonia gas is rapidly dissolved. In about two minutes remove the tube and withdraw the Bunsen burner from the flask; the liquid smells strongly of the gas.

Dissolve a little litmus in water in a test tube, add a drop of hydrochloric or sulphuric acid so as to just redden the solution. To this add some of the ammonia solution; the blue color is restored.

The readiest method of obtaining gaseous ammonia for the study of its properties consists in gently heating the strongest *liquor ammonia* in a retort provided with a

bent tube for collecting the gas by displacement, as shown in Fig. 5. The gas is evolved from the solution at a very low temperature, and may be collected unaccompanied by steam.

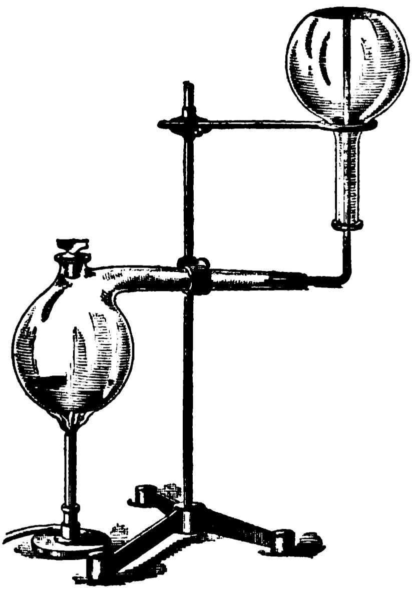

FIG. 5.

**14. Properties.** Ammonia is a colorless gas, and is readily distinguished by its very characteristic smell and its powerful alkaline action upon red litmus paper. It is considerably lighter than air, its specific gravity being .59. Subjected to a pressure of 6½ atmospheres at 10° or to a cold of −40°, it condenses to a colorless liquid of specific gravity .6362, which freezes at −75° and boils at −35.7°. It is soluble in water to an extraordinary degree, 1 volume of water at 0° absorbing 1,149 volumes of ammonia gas, forming the so called *aqua ammonia.* At 15°, 1 volume of water absorbs 783 volumes of the gas.

The solution of ammonia, which is quite an important article of commerce, may be prepared by conducting the gas into water contained in a two-necked bottle, the second neck being connected with a tube passing into another bottle containing water, too, in which any escaping ammonia may be condensed. The strength of the solution is inferred from its specific gravity, which is lower in proportion as the quantity of ammonia in the solution increases.

For instance, at 14° a solution having a specific gravity of .8844 contains 36 parts by weight of ammonia in 100 parts of the solution (*liquor ammoniæ fortissimus*); a solution having a

specific gravity of .9251 contains 20 per cent.; while one with a specific gravity of .9593 contains 10 per cent. of ammonia (British Pharmacopœia). The specific gravity is ascertained by comparing the weights of equal volumes of water and of the solution of the same temperature. For this purpose a light, stoppered bottle, or *pycnometer*, is used, capable of containing about 2 fluid ounces. This is thoroughly dried, and counterpoised in a balance by placing on the opposite pan tin foil or lead, which can be easily cut down to the proper weight. The bottle is then filled with a solution of ammonia, the temperature observed with a thermometer and carefully noted, the stopper inserted, and the bottle weighed. It is then well rinsed out, filled with distilled water, the temperature adjusted by placing the bottle either in warm or cold water, until the water is of exactly the same temperature as was the ammonia solution; then the bottle is carefully dried and weighed. The specific gravity is then obtained by dividing the weight of the ammonia solution by that of the water.

The **ammonia meter,** a form of hydrometer shown in Fig. 6, is a most convenient instrument for rapidly ascertaining the specific gravity of such liquids as are known to be lighter than water. It consists of a hollow glass float with a long stem, weighted with a bulb containing some heavy substance, such as mercury or shot, so that when placed in distilled water it may sink to 1.000° of the scale marked on the stem, this number representing the specific gravity of water. When placed in a liquid lighter than water, it must, of course, sink lower, in order to displace more liquid (since solids sink until they have displaced their own weight of liquid). By trying it in liquids of known specific gravities, the mark upon the scale to which it sinks may be made to indicate the specific gravity of the liquid. The ammonia meter generally has a scale so divided that it indicates at once the percentage weight of the ammonia solution in which it is dropped.


FIG. 6.

Chemically, ammonia gas has a strong but transient alkaline reaction upon vegetable colors, from which quality the name *volatile alkali*, sometimes given to ammonia, originates. Ammonia is a non-supporter of combustion and is non-inflammable at ordinary temperatures; but when heated it takes fire and burns with a greenish flame, water being produced and nitrogen set free, according to the equation:

$$\begin{array}{ccccccc} 4NH_3 & + & 3O_2 & = & 2N_2 & + & 6H_2O \\ \text{ammonia} & & \text{oxygen} & & \text{nitrogen} & & \text{water} \end{array}$$

**15. Carré's Freezing Apparatus.**—The readiness with which ammonia may be liquefied has led to its application in a freezing apparatus, which is shown in Fig. 7, invented and patented by M. Carré of Paris, France. In this apparatus the gas is generated by heating a concentrated solution of ammonia in a strong iron boiler $A$, and is liquefied by its own pressure in an iron receiver $B$ placed in cold water. When the boiler is taken off the fire and cooled in water, the liquefied ammonia evaporates very rapidly from the receiver back into the boiler, thereby producing so much cold that a vessel of water $C$, placed in spirit of wine contained in a cavity in the receiver, is at once congealed into ice.


FIG. 7.

To refrigerate large spaces by means of this machine, $C$ is filled with brine—which may be cooled below the freezing point of water without solidifying—and when this is cooled, it is circulated through pipes in the space to be refrigerated, and again returned to the freezing machine for a renewed cooling.

**16.** The student has already seen by Experiment 3 that ammonia restores the blue color to litmus paper reddened by

an acid. It neutralizes the strongest acids, and forms a well marked and most important series of salts. The composition of some of these is shown by the following equations:

| | | | | | | |
|---|---|---|---|---|---|---|
| $NH_3$ | $+$ | $HCl$ | $=$ | $NH_4Cl$ | . . . | $NaCl$ |
| ammonia | | hydrochloric acid | | ammonium chloride | | sodium chloride |
| $NH_3$ | $+$ | $HNO_3$ | $=$ | $NH_4NO_3$ | . . . | $NaNO_3$ |
| ammonia | | nitric acid | | ammonium nitrate | | sodium nitrate |
| $2NH_3$ | $+$ | $H_2SO_4$ | $=$ | $(NH_4)_2SO_4$ | . . . | $Na_2SO_4$ |
| ammonia | | sulphuric acid | | ammonium sulphate | | sodium sulphate |

The salts of sodium are given in the last column for the sake of comparison. The student will notice that the group $NH_4$ and sodium occupy corresponding places. Furthermore, this group may be expelled from one chemical compound and caused to enter another without decomposition.

The group $NH_4$ is one of the best and most striking examples of a *compound radical;* it behaves in so many compounds as though it were an element that it has received the name *ammonium*, for which the symbol $Am$ is frequently employed in complicated formulas. Ammonium chloride is written either $NH_4Cl$ or $AmCl$. Ammonium, however, cannot be isolated, but immediately decomposes into ammonia and free hydrogen. The solution of ammonia in water is sometimes conveniently represented as a hydrate; thus,

| | | | | |
|---|---|---|---|---|
| $NH_3$ | $+$ | $H_2O$ | $=$ | $NH_4HO$ |
| ammonia | | water | | ammonium hydrate |

This, again, is analogous in composition to sodium hydrate $NaHO$.

Ammonium hydrate produces in many cases the same chemical reaction as does either sodium or potassium hydrate. Thus, all these bodies produce the same precipitate of ferric hydrate $Fe_2(HO)_6$, from a solution of ferric chloride $Fe_2Cl_6$. The student is referred to the analytical section of this course for a more detailed account of these reactions.

The principle of the preparation of ammonia is simply, therefore, to displace it from a salt by the action of a stronger and non-volatile base, such as soda or lime.

**17. Composition of Ammonia.**—The composition of ammonia may be determined by introducing a given volume of the gas into a graduated tube over mercury, and passing electric sparks through it. It then decomposes and doubles in volume; and its alkalinity and its pungency, as well as its solubility, entirely disappear.

By eudiometry, that is to say, "by the use of a eudiometer" (see Fig. 19, *Inorganic Chemistry*, Part 1), the volumes of the constituents of ammonia may be ascertained in the following way:

Assuming that 100 cubic centimeters of ammonia are introduced into a eudiometer, then, on decomposing the ammonia by passing an electric spark through it, the ammonia will be found to have expanded to 200 cubic centimeters; if 100 cubic centimeters of oxygen are then added, and the electric spark again passed through this mixture, the 300 cubic centimeters will be reduced to 75 cubic centimeters, 225 cubic centimeters having apparently disappeared. Of these 225 cubic centimeters, two-thirds, or 150 cubic centimeters, must be hydrogen, and 75 cubic centimeters oxygen. Subtracting, now, this excess of oxygen from the original contents of the eudiometer, we have $100 - 75 = 25$ cubic centimeters, which, subtracted from the 75 cubic centimeters remaining in the eudiometer, leaves 50 cubic centimeters. This remainder is nitrogen. Hence, the 200 expanded volumes consist of 150 volumes of hydrogen and 50 of nitrogen; while ammonia gas consists of 3 volumes of hydrogen and 1 volume of nitrogen, the whole condensed into 2 volumes.

**18. Tests.**—Free ammonia may be easily detected by its well known penetrating odor, by its alkalinity, and by the fumes given when a rod moistened with hydrochloric acid is brought in close proximity. When combined, it may be set free by quicklime and then tested.

**19.** For many years, ammonia was the only compound of nitrogen with hydrogen that was known. Lately, two others have been discovered; namely, *diamine*, or *hydrazine* $N_2H_4$, and *hydroxylamine* $(OH)H_2N$. Both of these compounds are very closely related to ammonia. The former is a stable gas, possessing a peculiar, pungent odor and a great solubility in water. It reduces silver and copper salts to the metallic state, and forms a hydrate, $H_4N_2H_2O$. The latter, produced by reducing nitric acid with tin, forms salts analogous to those formed by ammonia, and these salts have a reducing action like that of diamine. *Hydrazoic acid* $HN_3$, discovered by Curtius in 1890, is a highly explosive gas.

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### SUMMARY.

**20.** Ammonia exists in traces in the atmosphere; it is formed by the decomposition of nitrogenous organic matter, and is manufactured from the watery distillate of the gas works.

Ammonia is a colorless gas, with characteristic odor, and may be readily liquefied by pressure or cold. It is very soluble in water. The gas is a non-supporter of combustion, and is non-inflammable at ordinary temperatures, but when heated it burns with a greenish flame. It is strongly alkaline to litmus solutions, and forms with acids a series of salts in which $NH_4$ occupies the place of a monad metal. This group $NH_4$ has received the name *ammonium* and the symbol *Am*; it does not exist in the free state, but breaks up into ammonia and hydrogen.

The composition is determined by decomposing the ammonia gas by electricity and estimating the hydrogen by combining it with oxygen.

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### LABORATORY DIRECTIONS.

**21.** In preparing ammonia from the chloride and lime, unless both are dried there is danger of breaking the flask by water condensing in the upper parts and trickling down

on the hot glass. It is a good plan to place two pieces of gauze under the flask and to keep the flame of the Bunsen burner *very small.* When collecting a gas by displacement, it is advisable to have a piece of cardboard closing the mouth of the jar, with a slit through it for the leading tube; this is kept on the mouth until a glass plate, serving as a cover, is exchanged for it.

When the end of the leading tube is placed in water (see Experiment 3), watch very carefully that the gas is not absorbed so rapidly as to cause the water to rise in the tube; should it have a tendency to do so, increase the heat by turning the Bunsen flame a little higher; if this should not prove effective enough, remove the beaker and draw the cork from the flask. In any case, remove *first* the beaker, and *then* the flame.

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## OXIDES AND ACIDS OF NITROGEN.

**22.** Five oxides of nitrogen are known to exist: those normally formed, in which the nitrogen has a valence of III and V; and those in which the nitrogen atoms are directly united, and may be viewed as free radicals. Their names, together with their corresponding acids, are as follows:

| *Oxides.* | | *Acids.* | |
|---|---|---|---|
| Hyponitrous oxide | $N_2O$ | Hyponitrous acid | $HNO$ |
| Nitrogen dioxide (nitrosyl) | $N'''_2O_2$ | | |
| Nitrous oxide | $N'''_2O_3$ | Nitrous acid | $HN'''O_2$ |
| Nitrogen tetroxide (nitryl) | $N^{v}_2O_4$ | | |
| Nitric oxide | $N^{v}_2O_5$ | Nitric acid | $HN^{v}O_3$ |

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### HYPONITROUS OXIDE.

*Formula $N_2O$. Density 21.99. Specific gravity 1.527. Molecular weight 43.98. One liter weighs 1.97 grams (21.99 criths).*

**23. History.**—Hyponitrous oxide, sometimes called also *nitrogen monoxide*, was discovered by Priestley in 1776. It

was more accurately examined by Davy in 1809, who discovered its exhilarating property. The gas became more widely known in 1845, when Wells began to use it as an anesthetic.

**24. Preparation.**—This gas may be prepared by the action of zinc on dilute nitric acid, the two being gently heated together; the reaction is a somewhat complex one, but may be represented by the following equation:

$$\underset{\text{nitric acid}}{10HNO_3} + \underset{\text{zinc}}{4Zn} = \underset{\text{hyponitrous oxide}}{N_2O} + \underset{\text{zinc nitrate}}{4Zn(NO_3)_2} + \underset{\text{water}}{5H_2O}$$

It is, however, much more easily obtained by decomposing ammonium nitrate by heat according to the equation:

$$(NH_4)NO_3 = N_2O + 2H_2O$$

The gas, being heavier than air, may be collected by displacement, or over warm water in a pneumatic trough. For its preparation an apparatus similar to that shown in Fig. 1, *Inorganic Chemistry*, Part 1, is used. It is advisable to place the generating flask in a sand bath and to apply a gentle heat only.

**25. Properties.**—Hyponitrous oxide is a colorless gas with a faint, sweetish smell and a distinctly sweet taste. It may be condensed to a liquid by a pressure of 32 atmospheres at 0°, or at ordinary pressures at −88°. The liquid freezes also by its own evaporation when allowed to escape into the open air, producing a snow-like mass. Hyponitrous oxide supports combustion nearly as vigorously as oxygen. A wax taper having a spark on its wick is relighted in it, much as in oxygen. Phosphorus as well as sulphur burn in it with great splendor, the gas being decomposed, and its oxygen uniting with the combustible substance forming oxides, while the nitrogen is liberated.

The gas is quite soluble in cold water, but only very sparingly in warm water. One hundred parts of water at 15° dissolve nearly 78 parts of the gas. It is still more soluble in alcohol and alkaline solutions.

Hyponitrous oxide behaves as an anesthetic when inhaled (i. e., it is a substance that causes insensibility to pain). It was with this gas that the property of anesthesia was discovered by Wells—a discovery everywhere acknowledged as the greatest for surgical work of the present century.

About 4 or 5 gallons of the gas are sufficient in most cases to produce total insensibility; before this stage is reached, it induces a state of intoxication, often accompanied by violent fits of laughter, and, owing to this exhilarating influence, it has received the popular name, *laughing gas*.

**26. Composition.**—The molecule of hyponitrous oxide $N_2O$ yields 1 molecule of nitrogen on decomposition, or any volume of this gas when decomposed yields its own volume of nitrogen.

The composition may be determined by exploding the gas in the eudiometer with excess of hydrogen:

$$N_2O + H_2 = N_2 + H_2O$$

A volume of nitrogen remains, which corresponds to the volume of the hyponitrous oxide taken, the diminution in volume being due to the hydrogen combining with the oxygen; it is necessary, however, to measure the excess of hydrogen that remains, in order to deduce from this experiment the composition of hyponitrous oxide.

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### HYPONITROUS ACID.

*Formula HNO. Molecular weight 30.97.*

**27.** By reducing a solution of potassium nitrate with sodium amalgam (a compound of sodium and mercury), potassium hyponitrite is obtained; and, by decomposing silver hyponitrite by hydrogen chloride, the free hyponitrous acid is obtained. It is strongly acid, rather stable, reduces permanganates, sets iodine free, and, on dehydration, yields hyponitrous oxide.

### NITROGEN DIOXIDE.

*Formula* $N_2O_2$.* *Molecular weight 59.94. One liter weighs 1.33 grams (14.98 criths).*

**28. History and Preparation.**—Nitrogen dioxide, though really discovered by Hales, was first thoroughly investigated by Priestley in 1772. It may be obtained by the action of copper on nitric acid; the reaction occurs without the application of heat. Hydrogen is probably first liberated, thus reducing some of the remaining acid. The reaction may be represented as follows:

$$\underset{\text{copper}}{3Cu} + \underset{\text{nitric acid}}{6HNO_3} = \underset{\text{copper nitrate}}{3Cu(NO_3)_2} + \underset{\text{nascent hydrogen}}{6H}$$

$$\underset{\text{nascent hydrogen}}{6H} + \underset{\text{nitric acid}}{2HNO_3} = \underset{\text{nitrogen dioxide}}{N_2O_2} + \underset{\text{water}}{4H_2O}$$

Or the two reactions may be stated in one equation; thus,

$$\underset{\text{copper}}{3Cu} + \underset{\text{nitric acid}}{8HNO_3} = \underset{\text{copper nitrate}}{3Cu(NO_3)_2} + \underset{\text{nitrogen dioxide}}{N_2O_2} + \underset{\text{water}}{4H_2O}$$

EXPERIMENT 5.—Take a flask and a delivery tube similar to that shown in Fig. 4, *Inorganic Chemistry*, Part 1, and place in it some copper clippings. Dip the cork in melted paraffin, and attach the leading tube to the delivery tube, with a small piece of rubber tubing about 2 inches long, so that the ends of both glass tubes are in close contact. Nitric acid rapidly corrodes both rubber and cork, so that we must avoid, as far as possible, the exposure of either to its influence—the paraffin protects the cork, and the leading tube is practically of glass throughout. Pour, then, on the copper a mixture of nitric acid and water, prepared by diluting the concentrate acid with its own volume of water. Bubbles of gas are evolved, and the generating flask rapidly fills with red fumes. These soon become lighter in color, and, as each bubble of gas rises through the water in the trough into the air, it assumes a dark-red tint. The air is now expelled from the generating flask, and the gas jar may be filled. Should the action slacken before the jar is entirely filled, add some more of the diluted nitric acid.

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* At ordinary temperatures the density of this gas is 14.985, showing that the molecule is $NO$, its molecular weight 29.97, and its specific gravity 1.039, under ordinary conditions; but to preserve the general form of the compounds of oxygen and nitrogen, it is considered as $N_2O_2$ for the present.

**29. Properties.**—Nitrogen dioxide is a colorless gas, which, on coming in contact with the air, combines with the oxygen and forms higher nitrogen compounds of a ruddy tint; from its affinity for oxygen it is difficult to either smell or taste it. The strong smell noticed during its preparation is that of these higher oxides, but not that of the nitrogen dioxide. It has almost the same specific gravity as air, namely, 1.039. It is more difficult to liquefy than hyponitrous oxide, its critical temperature being $-93°$, and its freezing point $-153°$, when it solidifies, resembling snow. It is much more stable than hyponitrous oxide, and may be subjected to even a red heat without suffering decomposition. In consequence of this property, it does not accelerate combustion. A lighted taper plunged into a jar filled with the gas is immediately extinguished. (The nitrogen dioxide prepared in the way described in Experiment 5, however, sometimes contains so much hyponitrous oxide that a taper burns in it brilliantly.)

Substances like phosphorus, however, which burn with sufficient evolution of heat to start decomposition of the dioxide, burn in it with great brilliancy if well ignited before they are introduced.

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### NITROUS OXIDE AND NITROUS ACID.

*Formulas $N_2O_3$ and $HNO_2$. Molecular weight of the oxide 75.90, of the acid 46.93.*

**30.** Nitrous oxide may be prepared by the reduction of nitric acid by arsenious oxide:

$$2HNO_3 + As_2O_3 = 2HAsO_3 + N_2O_3$$

By passing the evolved vapors through a freezing mixture, the nitrous oxide condenses to a rather unstable greenish-blue liquid, which reacts with water producing ***nitrous acid.***

Nitrous acid is a blue liquid, rather unstable at ordinary temperatures, but it may be preserved at a low temperature

unaltered. At ordinary temperatures it is readily decomposed into nitric acid, water, and nitrogen dioxide; thus,

$$3HNO_2 = HNO_3 + H_2O + N_2O_2$$

The salts of nitrous acid are known as ***nitrites.***

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**NITROGEN TETROXIDE.**

*Formula* $N_2O_4$ *or* $\left.\begin{matrix} NO_2 \\ NO \end{matrix}\right\} O$. *Molecular weight 91.86.*

**31.** Nitrogen tetroxide, or *free nitryl*, is generally prepared by heating perfectly dry lead nitrate.

$$2[Pb(NO_3)_2] = 2PbO + 2N_2O_4 + O_2$$

On passing the vapors through a freezing mixture, they condense to a liquid, or, if they are perfectly dry, to a white crystalline solid, which melts at $-9°$. As the temperature rises, the liquid changes its color. It passes from a light yellow to a deep orange until 22° are reached, when the liquid begins to boil, evolving an orange vapor, which at about 40° becomes almost black.

By the action of water, nitrogen tetroxide yields nitric and nitrous acids:

$$\left.\begin{matrix} NO_2 \\ NO_2 \end{matrix}\right\} + \left.\begin{matrix} H \\ H \end{matrix}\right\} O = \left.\begin{matrix} NO_2 \\ H \end{matrix}\right\} O + \left.\begin{matrix} NO \\ H \end{matrix}\right\} O$$

It is an energetic oxidizing agent, being used to oxidize sulphurous oxide in the sulphuric-acid process. It combines directly with chlorine to form *nitryl chloride* $NO_2Cl$.

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**NITRIC OXIDE.**

*Formula* $N_2O_5$. *Molecular weight 107.82.*

**32. History and Preparation.**—Nitric oxide, also known as *nitrogen pentoxide*, or *nitric anhydride*, was first prepared by Deville in 1849. It is formed by the action of phosphoric oxide on nitric acid, or, better, by the action of nitryl chloride upon silver nitrate at a temperature of 60°.

**33. Properties.**—Nitric oxide is a colorless, transparent solid, which crystallizes in right rhombic prisms. It melts at 30° and boils at 47°. It is very unstable, sometimes exploding spontaneously. It reacts energetically with water, producing nitric acid, according to the equation:

$$N_2O_5 + H_2O = 2HNO_3$$

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### HYDROGEN NITRATE, OR NITRIC ACID.

*Formula $HNO_3$. Density 31.445. Molecular weight 62.89. One liter of nitric acid vapor weighs 2.82 grams (31.445 criths).*

**34. History.**—Nitric acid was known to Geber, an alchemist, who lived in the eighth century; Raymond Lully in 1225 described a method of preparing it; and in 1785 Cavendish thoroughly investigated this compound and determined its composition synthetically.

**35. Occurrence.**—Nitric acid exists in small quantities in the atmosphere, from which it is separated by rain, which, consequently, usually exhibits, on analysis, traces of this acid. The salts of nitric acid, with soda and potash (sodium and potassium nitrates), are its most common sources.

Layers of potassium nitrate are found incrusting the soil in India, and of sodium nitrate in parts of Peru and Chile. These nitrates are produced by the oxidation of nitrogenous organic matter in the presence of the bases potash or soda. Potassium nitrate is also known as *saltpeter*, or *niter;* sodium nitrate is frequently called *Chile saltpeter*, or *cubic niter*, from the shape of its crystals.

**36. Preparation.**—Nitric acid is always produced by the distillation of a nitrate—generally sodium or potassium nitrate—with sulphuric acid. The two are mixed in a retort, and on the application of heat nitric acid, being volatile, distils over, leaving hydrosodium sulphate. The reaction may thus be represented:

$$\underset{\text{sodium nitrate}}{NaNO_3} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{nitric acid}}{HNO_3} + \underset{\text{hydrosodium sulphate}}{NaHSO_4}$$

EXPERIMENT 6.—Take a stoppered retort, clean and dry it thoroughly, and pour in about 20 grams (20 cubic centimeters of your measuring glass) of sodium nitrate through the tubulure (i. e., the hole for the

FIG. 8.

stopper). This is most easily done by taking a piece of paper and doubling it up as shown in Fig. 8; the sodium nitrate is placed on this and carefully transferred to the retort, which should be held as shown in the figure; on no account must any of the nitrate get into the neck of the retort.

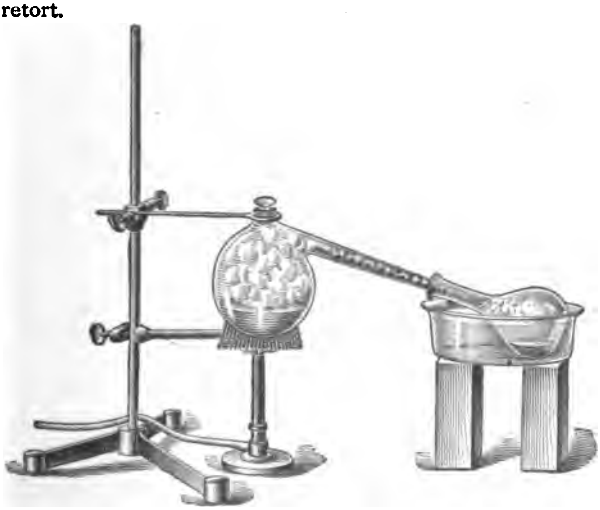

FIG. 9.

Next clean and drain a receiver, and introduce into it the beak of the retort, as shown in Fig. 9. Arrange the apparatus in the retort stand

with the receiver well under water in the pneumatic trough; the further the receiver is submerged in the cold water the better. To get up this arrangement satisfactorily, it may be necessary to raise the pneumatic trough somewhat; adjustments of this kind are best made by pieces of wood (blockings); the trough should be put in the proper place *first*, and then filled with water. Next pour in the retort about 15 cubic centimeters of concentrated sulphuric acid, replace its stopper, and apply heat carefully with the Bunsen burner.

The nitrate soon melts, the retort becomes filled with brownish-red fumes, and a pale yellow liquid $HNO_3$ distils over into the receiver.

**37. Properties.**—Nitric acid, when pure, is a colorless, fuming, corrosive, and strongly acid liquid, which is always associated with more or less water; but usually has a faint yellow tinge, owing to the presence of some of the lower oxides of nitrogen, produced by its partial decomposition. Its specific gravity is 1.54 or less, depending on the amount of water present; cooled to $-55°$, the acid freezes, and heated to 86°, it boils, undergoing partial decomposition. It is also readily decomposed by light.

Chemically, it is a powerful oxidizing agent, acting on most of the metals with great vigor; gold and platinum, however, are not affected by it. Nitrogenous animal substances, such as parchment, silk, horn, and wool are colored yellow by nitric acid. Many non-nitrogenous vegetable substances, such as cotton, sugar, glycerine, etc., are converted by it into violently explosive bodies.

The commercial nitric acid—sold as *aqua fortis*—is of two sorts, called *single* and *double*. Double aqua fortis has a specific gravity of 1.42, and contains about 67 per cent. of $HNO_3$; the single has a specific gravity of 1.29, and contains about 46 per cent. of the pure acid.

Nitric acid, being a monobasic acid, can only form normal salts, which may be represented by the formula $M(NO_3)$, $M$ standing for any monad metal. When free, nitric acid reddens litmus powerfully, bleaches indigo solutions, and evolves red fumes on introducing a little copper. These reactions are also obtained from nitrates after treatment with sulphuric acid. Moreover, nitrates deflagrate (i. e., undergo a vigorous combustion) when thrown on burning charcoal.

**38. Uses.**—Nitric acid finds wide use in the arts. It is employed for etching on metals, for oxidizing various substances, for forming certain substitution products, such as nitrobenzol and picric acid, and for the preparation of explosives, such as guncotton, nitroglycerin, etc.

All the metals in common use are attacked by nitric acid, except gold, platinum, and aluminum, so that this acid is employed to distinguish and separate the first two metals from others of less value. The ordinary method of ascertaining whether a trinket is made of gold consists in touching it with a glass stopper moistened with nitric acid, which leaves gold untouched, but colors base alloys blue, from the formation of copper nitrate. The *touchstone* allows this method of testing to be applied with great accuracy. It consists of a species of black basalt, obtained chiefly from Silesia. If a piece of gold is drawn across its surface, a golden streak is left, which is not affected by moistening with nitric acid; while the streak left by brass, or any similar base alloy, is rapidly dissolved by the acid. Experience enables an operator to determine, by means of the touchstone, pretty nearly the amount of gold present in an alloy, comparison being made with streaks left by gold alloys of known composition.

**39. Aqua Regia.**—Neither nitric acid nor hydrochloric acid alone has the property of dissolving gold; but a mixture of one measure of nitric and three measures of hydrochloric acid readily dissolves gold. The name *aqua regia* has been bestowed upon this mixture. This property of dissolving gold depends on the presence of free chlorine, which is liberated in the action of the acids upon each other, as shown in the following equation:

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$$

**40. Action of Nitric Acid and Nitrates.**—The action of nitric acid on the metals is generally more complex than the action of hydrochloric or sulphuric acid; the nascent hydrogen, displaced by the metal, attacks the remaining nitric acid and forms water, liberating one or more of the

lower oxides of nitrogen. The particular oxide evolved, and the proportions of each present in a mixture, depend on the metal used, the degree of concentration of the acid, and various other causes.

EXPERIMENT 7.—To some of the nitric acid obtained by Experiment 6, add a few pieces of copper clippings; notice that a violent action goes on, ruddy fumes are evolved, and a green solution of copper nitrate is formed.

Nitric acid is a monobasic acid, its salts being known as *nitrates*. These nitrates may be prepared either by acting on the metal, as with copper in Experiment 5, or by adding the acid to an oxide or carbonate.

EXPERIMENT 8.—Take some strong nitric acid, place it in a beaker, and add some solid ammonium carbonate in small quantities, until it no longer causes effervescence; the liquid will then have an alkaline reaction to litmus paper. Add now, nitric acid, drop by drop, until the solution is neutral; place this away for a week in an evaporating basin; at the end of that time long needles of ammonium nitrate will have crystallized out. The salt may be preserved in a bottle for future use.

The nitrates, like the acid from which they are derived, are powerful oxidizing agents; potassium nitrate is used as a source of oxygen in gunpowder, which is a mixture of that compound with sulphur and charcoal.

If charcoal is dropped into melting potassium nitrate, it takes fire and burns with great brilliancy.

EXPERIMENT 9.—Melt some potassium nitrate in a test tube, and drop in a fragment of charcoal; it burns with the evolution of carbon dioxide. *The experimenter should hold the mouth of the tube away from his body, as sometimes the red-hot piece of charcoal jumps out of the tube.*

By heat, nitric acid and all the nitrates are decomposed; the metallic oxides remain, while the oxides of nitrogen, and oxygen also, are driven off. A good example of this is given in the reaction that takes place when nitric acid is passed through a red-hot tube of clay:

$$\underset{\text{nitric acid}}{4HNO_3} = \underset{\text{water}}{2H_2O} + \underset{\text{nitrogen tetroxide}}{2N_2O_4} + \underset{\text{oxygen}}{O_2}$$

or, when potassium nitrate is heated, the following change occurs:

$$\underset{\text{potassium nitrate}}{2KNO_3} = \underset{\text{potassium nitrite}}{2KNO_2} + \underset{\text{oxygen}}{O_2}$$

**41. Determination of the Composition of Nitric Acid.**—A definite weight, say 10 grams, of pure lead oxide is taken, 5 grams of nitric acid mixed with it, and a gentle heat applied as long as vapor of water escapes:

$$PbO + 2HNO_3 = H_2O + Pb(NO_3)_2$$

Say that the residue weighs 14.27 grams; then by deducting 14.27 grams, the weight of the lead oxide and lead nitrate, from 15 grams, the weight of the lead oxide and nitric acid, the water that has been expelled, or .73 gram, is obtained, which corresponds with $\frac{.73}{9}$, or .08 gram of $H$.

The mixture of lead nitrate and excess of lead oxide (forming the residue) is then strongly heated in a tube containing copper, when

$$Pb(NO_3)_2 + Cu_5 = PbO + 5CuO + N_2$$

The nitrogen thus evolved is collected and measured. Suppose that 885.9 cubic centimeters of $N$ are obtained; these would (since 1,000 cubic centimeters weigh 1.255 grams) weigh 1.112 grams.

Hence, in 5 grams of nitric acid we find 1.112 grams of $N$, .08 gram of $H$, and by difference 3.808 grams of $O$. Dividing these numbers by their atomic weights (14, 1, and 16, respectively), we obtain .08 of $N$, .08 of $H$, and .24 of $O$, or 1 atom of $H$ to 1 atom of $N$ and 3 atoms of $O$. This would give for the molecule of nitric acid $HNO_3$, $1+14+48 = 63$, a result corresponding closely to the molecular weight given (62.89).

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## SUMMARY.

**42.** Five oxides of nitrogen are known, three of which form acids.

Nitric acid is the most important. Traces of it exist in the atmosphere. It is manufactured from nitrates by distillation

with sulphuric acid. It is a powerful oxidizing agent; though it attacks most of the metals, it has no action on gold or platinum. These metals, however, may be dissolved by aqua regia.

Hyponitrous oxide, or laughing gas, is usually prepared by heating ammonium nitrate. It is colorless, has a faint, sweetish odor, and distinct sweetish taste; is somewhat soluble in water, is non-inflammable but supports combustion. It acts as an anesthetic.

Nitrogen dioxide is prepared by the action of copper on nitric acid. It is colorless, but on exposure to air immediately becomes red by combination with oxide. It is more stable than hyponitrous oxide, and does not support combustion, unless the heat is sufficient to decompose it into oxygen and nitrogen.

The other oxides and acids are comparatively unimportant.

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### LABORATORY DIRECTIONS.

**43.** Wooden blocks for the adjustment of the height of different pieces of apparatus are always useful in a laboratory, and should be at hand. Blocks 6 inches square are of a convenient size, and the following thicknesses may be kept on hand: $\frac{1}{2}$, 1, 2, 3, and 4 inches. They may be obtained at very small expense from any carpenter.

The flask used for the preparation of hyponitrous oxide (see Art. **24**) should not be less than 8 ounces, as otherwise some of the melting nitrate may froth up and choke the tube; should any do so, immediately remove the light, as the continued evolution of gas might burst the flask. If the applied heat is too great the gas comes over impure; and if it is cloudy in the jar, that may be looked on as a sign that the heat must be moderated.

The action of copper on nitric acid (Experiment 5) does not always start immediately; when this is the case apply a very gentle heat to the flask until the action commences. It is likely then to proceed with great rapidity; a large generating flask should therefore be used. If the gas is coming over

too fast, pour in a little water; this will render the action less violent. The cork and tubing used should be washed at once after use. The directions for the protection of the cork and tubing are important; if a long piece of rubber tubing is used as connection, the tubing is not only destroyed, but also becomes stopped up with the products of corrosion. It is a good plan, in this particular case, to have the leading tube bent out of one piece of glass tubing; but, if there is a joint, provided the ends of both glass tubes touch each other, as directed, it will not matter much.

In adding ammonium carbonate to nitric acid (Experiment 8), do not throw it in in the form of fine powder, as the action is then so violent that it is likely to overflow the beaker. Pieces about the size of peas are the most convenient for this experiment.

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## PHOSPHORUS.

*Symbol P. Atomic weight 30.96. Density 61.92. Valence III and V. Specific gravity 1.83. Molecular weight 123.84. One liter of phosphorus vapor weighs 5.55 grams (61.92 criths).*

**44. History.**—Phosphorus was discovered by Brandt, in 1669, who ignited evaporated urine in a closed vessel. One hundred years later, in 1769, Gahn and Scheele discovered it in bones, and in 1775 proposed a method of preparing it from them.

**45. Occurrence.**—Phosphorus never occurs uncombined in nature, but is found abundantly combined in the form of phosphate of calcium $Ca_3(PO_4)_2$, which is contained in the minerals *coprolite*, *phosphorite*, and *apatite*, and occurs diffused, though generally in small proportions, through all soils on which plants will grow; for phosphorus, probably in the form of phosphate of calcium, is an essential constituent of the food plants, and especially of the cereal plants, which form so large a proportion of the food of animals. The seeds of such plants are especially rich in the phosphates of calcium and magnesium.

Animals feeding on these plants still further accumulate the phosphorus, for it enters, chiefly in the form of calcium phosphate, into the composition of almost every solid and liquid in the animal body, and is especially abundant in the bones, which contain about three-fifths of their weight of calcium phosphate.

**46. Preparation.**—Phosphorus is the only element for the ordinary preparation of which animal substances are employed. It is prepared by acting on burned bones, with sulphuric acid, leaching off the resulting liquid, evaporating it to dryness, and distilling the residue with charcoal. The earthy matter of bones consists of calcium phosphate $Ca_3(PO_4)_2$, and, by treating this with sulphuric acid, hydrocalcium phosphate results, according to the following equation:

$$\underset{\text{calcium phosphate}}{Ca_3(PO_4)_2} + \underset{\text{sulphuric acid}}{2H_2SO_4} = \underset{\text{calcium sulphate}}{2CaSO_4} + \underset{\text{hydrocalcium phosphate}}{H_4Ca(PO_4)_2}$$

The hydrocalcium phosphate is leached off from the insoluble calcium sulphate, and by evaporating the solution to dryness, is converted into a calcium metaphosphate; thus,

$$H_4Ca(PO_4)_2 = Ca(PO_3)_2 + 2H_2O$$

and the calcium metaphosphate distilled with charcoal gives phosphorus and calcium phosphate again, according to the equation:

$$3Ca(PO_3)_2 + 10C = Ca_3(PO_4)_2 + 10CO + P_4$$

In the manufacture of phosphorus on the large scale, the bones, previously burned and powdered very finely, are mixed with two-thirds of their weight of strong sulphuric acid diluted with 18 to 20 parts of water, well stirred, and allowed to stand for about 12 to 14 hours. The clear liquid is strained off the sediment, which consists of calcium sulphate, or gypsum, evaporated in a pan to a syrupy consistence, mixed with one-fifth of its weight of charcoal, finely powdered, and heated to redness. The dry mass is then

placed in earthen retorts *B*, *B*, Fig. 10, and these are slowly raised to bright redness in the furnace *A*, when the phosphorus distils over and condenses in the receivers *C*, *C*.

Theoretically, the bone ash should yield about 11 per cent. of phosphorus, but practically hardly more than from 8 per cent. to 9 per cent. is obtained.

The crude phosphorus is purified by enclosing it in a chamois-skin sack, and strongly compressing it under water

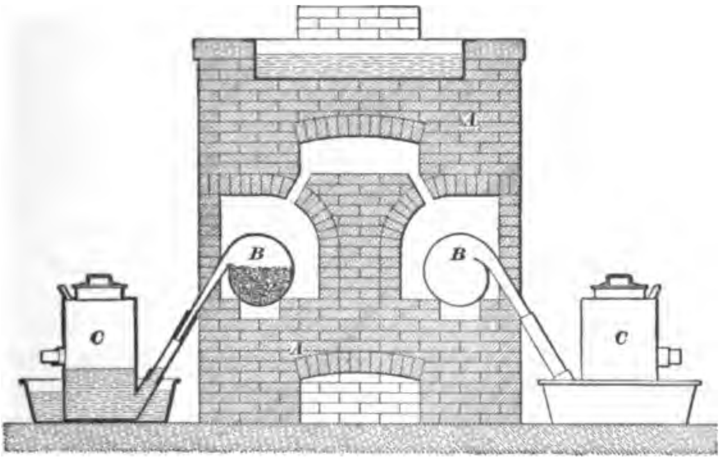


FIG. 10.

at 50°; the phosphorus passes through the leather and collects under the water. It is molded into sticks by being drawn up into slightly conical glass tubes, which are then plunged into cold water. The phosphorus solidifies and is easily drawn from the tubes.

**47. Properties.**—Phosphorus is distinguished from all the other elements that have been so far considered, in that it has 4 instead of 2 atoms in the molecule. This, however, does not mean that the molecule of phosphorus is twice the normal volume of other elements, which would be a contradiction of Avogadro's law, but simply that, with the same molecular volume as other bodies in the gaseous state, the phosphorus molecule contains 4 atoms.

Phosphorus is an almost colorless (slightly yellow) and transparent solid, specific gravity 1.83, with a consistency of beeswax at ordinary temperatures, and may be easily cut with a knife. At the freezing point it becomes considerably harder and more brittle; it then shows, on being broken, evidences of crystalline structure. Phosphorus melts at 44° to a colorless liquid, and boils at 290°, yielding a colorless vapor of specific gravity 4.355. It crystallizes from its solution in carbon disulphide in the form of the regular dodecahedron. When exposed to the air, phosphorus is seen to evolve small quantities of smoke, and in the dark is distinctly luminous, though a trace of naptha or oil of turpentine in the air prevents this phenomenon. From this property it has received its name, which signifies "light bearer." It is not soluble in water, but dissolves readily in carbon disulphide, in phosphorus chloride, in alcohol, in ether, and in certain volatile oils.

Phosphorus is characterized by its great inflammability; at a temperature of about 45°, a little over its melting point, it takes fire, and burns brightly with the formation of phosphoric oxide. Phosphorus is easily ignited by a slight amount of friction.

Owing to the readiness with which it undergoes oxidation, phosphorus is always kept under water, which liquid it does not decompose. Phosphorus is violently poisonous, and kills by depriving the blood of oxygen. Oil of turpentine is the best antidote.

**48. Red, or Amorphous, Phosphorus.**—In addition to the yellow variety, phosphorus occurs in another totally distinct form, known as *red*, or *amorphous*, *phosphorus*. Schrötter, in 1848, discovered that, by heating ordinary phosphorus to 300° in a gas that had no direct action on this element, the phosphorus was converted into a chocolate-red powder, possessing properties entirely different from those previously exhibited.

This modification differs most remarkably from the yellow

kind. Its specific gravity is 2.14. It is insoluble in the ordinary solvents of phosphorus, but may be dissolved in metallic lead by being heated in a sealed tube together with this metal. On cooling, it crystallizes out in acute rhombohedral crystals having a metallic luster, an almost black color, and a specific gravity of 2.34. It has no odor, is not luminous and, when exposed to air, does not oxidize, and, consequently, need not be preserved under water. It remains solid up to a temperature beyond 250°, and does not take fire when heated in the air until 260° is reached. At this point it becomes changed into the yellow variety, and burns.

If the heating is conducted in a retort filled with carbon dioxide, so as to prevent combustion, the same weight of yellow phosphorus is produced, proving most convincingly that the two varieties are only allotropic modifications of one and the same element. Further, both, on being burned, produce the same weight of phosphorus pentoxide $P_2O_5$.

The change from the yellow to the red variety is much accelerated by the presence of iodine in small quantities.

EXPERIMENT 10.—Place a piece of phosphorus, of about the size of a pea, in a test tube; drop on it a very small fragment of iodine; combination at once occurs, with the formation of a small quantity of phosphorous iodide. Heat gently; the phosphorus melts and takes fire, but soon exhausts the whole air in the tube. Continue to warm gently for a little time, and most of the phosphorus will be seen to become of a dark-red color. Cork up the test tube and allow it to cool. When quite cold, pour some carbon disulphide into another tube, *and put the bottle away*, and then from the tube pour the disulphide on the altered phosphorus. Cork up again, and allow the tube to stand for some time, giving it an occasional shake. Pour off the carbon disulphide, and a residue of amorphous phosphorus remains.

**49. Uses.**—Phosphorus is extensively used in the manufacture of matches, and also finds employment in medicine and the production of rat poison. Its spectrum is characterized by two green lines, readily seen in the flame of hydrogen that has been passed over phosphorus.

**50.** Lucifer matches (the common "sulphur matches") are made by tipping the wood with either sulphur, wax, or paraffin, to convey the flame, and afterwards with the match composition, which is generally composed of saltpeter or potassium chlorate, phosphorus, red lead, and glue, and depends for its action on the easy inflammation by friction of phosphorus when mixed with oxidizing agents like saltpeter $KNO_3$, potassium chlorate $KClO_3$, or red lead $Pb_3O_4$; the glue only serves to bind the composition together and attach it to the wood. The composition used by different makers, naturally, varies much in the nature and proportions of the ingredients. In this country and England, potassium chlorate is the most commonly employed as the oxidizing agent, such matches usually kindling with a slight detonation; but the German manufacturers prefer either potassium nitrate or lead nitrate, together with lead dioxide, which produce *silent matches.*

Sulphide of antimony is also used in those compositions in which a part of the phosphorus is employed in the red form, and fine sand or powdered glass is very commonly added, to increase the susceptibility of the mixture to inflammation by friction.

The match composition is colored either with ultramarine blue, Prussian blue, or vermilion. In preparing the composition, the glue and the niter or chlorate are dissolved in hot water; the phosphorus is then added and carefully stirred in until intimately mixed, the whole being kept at a temperature of about 38°. The fine sand and coloring matter are then added, and, when the mixture is complete, it is spread out upon a stone slab heated by steam, and the sulphured ends of the matches are dipped into it.

The so called *Swedish* or *safety matches*, which only ignite by rubbing upon the sides of the box in which they are sold, are tipped with a mixture of antimony sulphide, potassium chlorate, and powdered glass, which is not sufficiently sensitive to be ignited by any ordinary friction, but inflames at once when rubbed upon the red phosphorus mixed with glass, which coats the rubbing surfaces on both sides of the box.

## PHOSPHORUS AND HYDROGEN.

**51.** Three compounds of phosphorus and hydrogen are known: $H_3P$, a gaseous compound; $H_4P_2$, a liquid compound; $H_2P_4$, a solid compound.

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### HYDROGEN PHOSPHIDE, OR PHOSPHINE.

*Formula $H_3P$. Density 16.98. Specific gravity 1.17. Molecular weight 33.96. One liter weighs 1.52 grams (16.98 criths).*

**52. History.** — Hydrogen phosphide, or *phosphine*, which, according to some authors, is also sometimes called *phosphureted hydrogen*, was discovered in 1783 by Gengembre, and further investigated by Heinrich Rose in 1832.

**53. Preparation.** — On boiling a strong solution of caustic soda or potash with phosphorus, a spontaneously

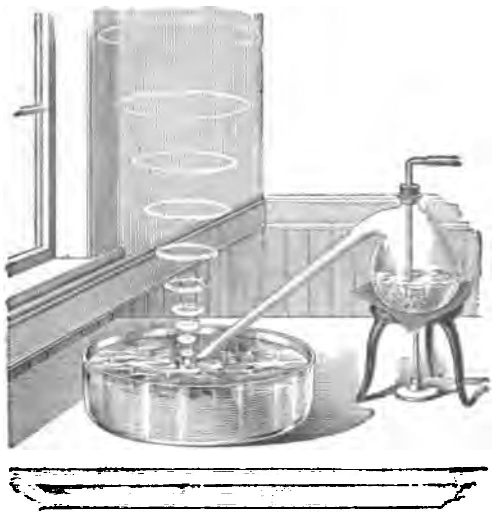

FIG. 11.

inflammable gas is evolved, having the odor of putrid fish, and approximately the composition $H_3P$. This gas is phosphine.

EXPERIMENT 11.—Fit up a retort with a delivery tube, with its end leading into a pneumatic trough, as shown in Fig. 11, and arrange the whole in a retort stand. Introduce into the retort a few fragments of caustic potash, together with some small pieces of phosphorus and a little water. Pass coal gas through the tubulure, so as to completely displace the air; then close the tubulure tightly. Gently heat the retort; bubbles of gas soon rise and displace the coal gas. In a short time, each bubble, as it rises to the surface of the water in the pneumatic trough, bursts into flame and generates an extremely beautiful ring of white smoke, which rotates on its circular axis as it ascends. If the air of the room is still, several of these rings will follow each other up to the ceiling.

The reaction by which phosphine is thus produced, is a somewhat complicated one, but may be expressed thus:

$$\underset{\text{phosphorus}}{P_4} + \underset{\substack{\text{potassium}\\\text{hydrate}}}{3KHO} + \underset{\text{water}}{3H_2O} = \underset{\substack{\text{potassium}\\\text{hypophosphite}}}{3KH_2PO_2} + \underset{\text{phosphine}}{H_3P}$$

In addition to phosphine $H_3P$, traces of $H_4P_2$ are formed. It is the presence of these that causes the gas to inflame spontaneously. If the gas is collected in a jar, on standing, it loses this property of spontaneous inflammation, because the second phosphide $H_4P_2$ suffers decomposition.

In the above mentioned method of preparing the gas, milk of lime (i. e., lime suspended in water) may be employed instead of caustic potash.

**54. Properties.**—Phosphine is a colorless gas with an unpleasant odor of putrid fish. It is sparingly soluble in water, is condensable to a liquid, and is neutral in its reactions. It takes fire readily at 100°, burning with a brilliant flame, but is not a supporter of combustion.

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## OXIDES AND ACIDS OF PHOSPHORUS.

**55.** The normal oxides and acids of phosphorus form a parallel series with those of nitrogen. The known members of the series are the following:

| *Oxides.* | | *Acids.* | |
|---|---|---|---|
| Phosphorous oxide | $P_2'''O_3$ | — | |
| Phosphoric oxide | $P_2^vO_5$ | Hypophosphorous acid | $HP^vO_2H_2$ |
| | | Phosphorous acid | $H_2P^vO_3H$ |
| | | Phosphoric acid | $H_3P^vO_4$ |
| | | Metaphosphoric acid | $HP^vO_3$ |

### PHOSPHORIC OXIDE.

*Formula* $P_2O_5$. *Molecular weight 141.72.*

**56. Preparation.**—Phosphoric oxide—*phosphorus pentoxide*, according to some authors—is always the product of the rapid combustion of phosphorus in the air or in oxygen. The reaction, which is synthetic, may be expressed by the following equation:

$$P_4 + 5O_2 = 2P_2O_5$$

EXPERIMENT 12.—Place under a large bell glass a flat china dish containing sulphuric acid, and leave this standing for about an hour or two, so as to dry thoroughly the air under the bell jar. Then remove the dish carefully, without disturbing the air within the jar. A small fragment of phosphorus, about the size of a very small pea, and carefully dried between two pieces of blotting paper, is placed in a china saucer standing on a good sized plate of glass and is introduced under the bell jar, the phosphorus having been kindled with a hot wire. White fumes will fill the jar, come together, and fall into the saucer and on the glass plate, resembling in appearance a miniature snow storm.

**57. Properties.**—Phosphoric oxide is, as has been demonstrated by Experiment 12, a snow-like, amorphous substance. It is fusible at red heat and is readily volatilized. When plunged into water it hisses, like a red-hot iron, but it does not at once entirely dissolve, as a few flakes of metaphosphoric acid $HPO_3$ always remain suspended in the liquid for some time. Its great feature is its attraction for water; left exposed to the air for a few minutes only, it deliquesces entirely, becoming converted into phosphoric acid. It is often used in laboratories as a dehydrating agent, and will even remove water from oil of vitriol (Nordhausen sulphuric acid).

### PHOSPHORIC ACID, OR TRIHYDROGEN PHOSPHATE.

*Formula* $H_3P^vO_4$. *Molecular weight* 97.8.

**58. Preparation.**—Phosphoric acid is obtained by the action of boiling water on phosphoric oxide:

$$\underset{\text{phosphoric oxide}}{P_2O_5} + \underset{\text{water}}{3H_2O} = \underset{\text{phosphoric acid}}{2H_3PO_4}$$

A method commonly employed for the preparation of phosphoric acid consists of oxidizing phosphorus with nitric acid, when the following reaction occurs:

$$\underset{\text{phosphorus}}{P_4} + \underset{\text{nitric acid}}{10HNO_3} + \underset{\text{water}}{H_2O} = \underset{\text{phosphoric acid}}{4H_3PO_4} + \underset{\text{nitrogen trioxide}}{5N_2O_3}$$

The solution, on evaporation at the close of the reaction, yields a viscid liquid, from which colorless crystals of phosphoric acid may be obtained.

EXPERIMENT 13.—Take a beaker about 6 inches high, and pour in it 30 cubic centimeters of concentrated nitric acid and 15 cubic centimeters of water. Cut a few small pieces of phosphorus and drop them into the diluted acid. Heat the whole gently; nitrous fumes are evolved, and the phosphorus is dissolved. Should the action cease before the whole of the phosphorus has disappeared, add a little more acid. At the close of the reaction, evaporate the liquid until it attains a temperature of 150°. Phosphoric acid remains.

Commercially, the acid, which, however, is somewhat impure, is prepared by treating bone ash (calcium phosphate) with sulphuric acid.

**59. Properties.**—Phosphoric acid thus prepared is a syrupy liquid, which by evaporation gives hard, transparent, prismatic crystals, which deliquesce in the air. Their solution is intensely acid.

From ammoniacal solutions of magnesium sulphate, it precipitates white, crystalline, ammonium-magnesium phosphate, sometimes called *triple phosphate*. With silver nitrate, phosphoric acid, when neutralized by ammonia, gives yellow silver phosphate. On heating the aqueous solution of phosphoric

acid to 213°, it gives diphosphoric acid, and, on raising the temperature still higher, metaphosphoric acid is obtained.

This acid contains 3 atoms of replaceable hydrogen, and is, consequently, tribasic. It is, therefore, capable of forming acid, normal, and double salts. In the normal salts the whole 3 atoms of hydrogen are replaced by metals; but in the acid salts either 1 or 2 atoms of hydrogen may remain. The following series is illustrative of the various salts of phosphoric acid:

*Acid Salts.*

| | |
|---|---|
| Dihydrosodium phosphate | $H_2NaPO_4$ |
| Hydrodisodium phosphate | $HNa_2PO_4$ |
| Hydrocalcium phosphate | $HCa''PO_4$ |

*Normal Salts.*

| | |
|---|---|
| Potassium phosphate | $K_3PO_4$ |
| Barium phosphate | $Ba''_3(PO_4)_2$ |
| Bismuth phosphate | $Bi'''PO_4$ |

*Double Salts.*

| | |
|---|---|
| Ammonium-magnesium phosphate | $(NH_4)Mg''(PO_4)$ |
| Potassium-barium phosphate | $KBa''(PO_4)$ |

The acid and normal salts are sometimes called primary, secondary, or tertiary salts, according as 1, 2, or 3 hydrogen atoms are replaced to form them.

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### MONOHYDROGEN PHOSPHATE, OR METAPHOSPHORIC ACID.

*Formula $HPO_3$. Molecular weight 79.84.*

**60. History and Preparation.**—In 1833, Graham showed that phosphoric acid loses water on being strongly heated, and that, on cooling, it becomes a transparent ice-like solid, which he named *glacial phosphoric acid:*

$$H_3PO_4 - H_2O = HPO_3$$

This same acid is also prepared by dissolving phosphoric oxide in cold water:

$$P_2O_5 + H_2O = (HPO_3)_2$$

Metaphosphates are produced by igniting acid phosphates that possess two hydrogen atoms,

$$H_2NaPO_4 - H_2O = NaPO_3$$

or that have two atoms of volatile base,

$$\underset{\text{hydroammonium sodium phosphate}}{H(NH_4)NaPO_4} = \underset{\text{ammonium hydrate}}{H(NH_4)O} + \underset{\text{sodium metaphosphate}}{NaPO_3}$$

By decomposing metaphosphates the acid is obtained.

**61. Properties.**—Metaphosphoric acid is a transparent, colorless, hard, and glassy mass, which, though very soluble in water, is not crystallizable. Dissolved in water, it forms a strongly acid solution, which gradually takes up water from the air and forms trihydrogen phosphate. It possesses the property of coagulating albumin—a property that phosphoric acid does not possess—and gives a white precipitate with silver nitrate. Being monobasic, it forms but one class of salts. It is distinguished by a remarkable tendency to produce polymeric forms, called di-, tri-, tetra-, and hexa-metaphosphates, respectively.

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### DIPHOSPHORIC, OR PYROPHOSPHORIC ACID.

*Formula* $H_4P_2O_7$. *Molecular weight 177.64.*

**62.** In 1826, Clark discovered a variety of phosphoric acid intermediate between the two forms already described, produced by heating a solution of the tribasic acid to 213°, and which he named *pyrophosphoric acid.* Two molecules of the trihydrogen phosphate together lose one of water:

$$(H_3PO_4)_2 - H_2O = H_4P_2O_7$$

Pyrophosphates, more generally known as *diphosphates*, are produced by igniting a phosphate that has 1 atom of volatile base:

$$\underset{\text{hydrodisodium phosphate}}{(HNa_2PO_4)_2} - \underset{\text{water}}{H_2O} = \underset{\text{sodium diphosphate}}{(Na_2P)_2O_7}$$

Diphosphoric acid generally occurs in solution, but may be obtained by evaporation at 213° as a soft glass or in semicrystalline masses. Its solution is strongly acid, does not coagulate albumin, and precipitates white silver nitrate. Being tetrabasic, diphosphoric acid forms a large series of acid, normal, and double salts.

On boiling its solution, it takes up 1 molecule of water and becomes trihydrogen phosphate; on igniting it, it loses 1 molecule of water, becoming monohydrogen phosphate.

**63. Aldehydic Phosphoric Acids.**—Two other acids of pentad phosphorus are known, which, as they resemble closely the aldehydes of organic chemistry, may be called *aldehydic acids*. These are commonly known as *phosphorous* and *hypophosphorous acids*. Phosphorous acid has the formula $H_2(PO_3H)$, is dibasic, and forms so called phosphites. It is prepared by decomposing the trichloride with water:

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3$$

By evaporating this solution under diminished pressure, the phosphorous acid separates in crystals, which deliquesce in the air, and dissolve readily in water. It fumes at 70° and at a higher temperature decomposes into $PH_3$ and $H_3PO_4$:

$$4H_3PO_3 = PH_3 + 3H_3PO_4$$

The acid absorbs oxygen from the air and is converted into phosphoric acid. It is therefore a reducing agent, and precipitates many of the metals from their solutions.

Hypophosphorous acid has the formula $H(PO_2H_2)$, is monobasic, and is obtained by decomposing barium hypophosphite with sulphuric acid. Hypophosphites are formed by boiling phosphorus in alkaline solutions.

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### PHOSPHOROUS OXIDE.

*Formula $P_2O_3$. Molecular weight 109.8.*

**64. Preparation and Properties.**—Phosphorous oxide is the product of imperfect combustion of phosphorus in dry air.

To obtain phosphorous oxide, ordinary phosphorus is placed in a tube (Fig. 12), drawn to a point at one end and at the other connected with a thinner glass tube known as an aspi-

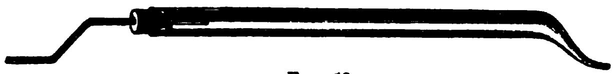

FIG. 12.

rator, by means of which air may be drawn through the tube. On heating the tube, the phosphorus takes fire, and a bulky amorphous deposit of phosphorous oxide collects beyond it in the tube. The white flakes are readily volatile and have an alliaceous* odor. They are deliquescent and dissolve in water with a hissing noise, forming an acid solution. The constitution of this compound is not known, but it can hardly be considered normal, since it does not give the normal acid by the action of water.

No acid of triad phosphorus is definitely known.

**65.** It is claimed that other oxides of phosphorus have been prepared, but as they are of no importance and little is known of them, they will not be treated here.

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### SUMMARY.

**66.** Phosphorus does not occur uncombined in nature, but abundantly as a constituent of various rocks. It is obtained from phosphates by reduction with carbon, is inflammable, and exists in two forms, which differ widely from each other in properties.

Hydrogen phosphide is prepared by heating phosphorus with caustic-potash solution, and is an inflammable gas with the odor of putrid fish.

Phosphoric acid is formed either by the action of boiling water upon phosphoric oxide, or by the oxidation of phosphorus by nitric acid. This acid is tribasic, and forms an extended series of salts.

* Alliaceous, or "garlic-like," is derived from the Latin word *allium*, 'garlic."

### LABORATORY DIRECTIONS.

**67.** The student will already be sufficiently familiar with the properties of phosphorus to know that it requires extremely careful handling. Never touch it with your fingers; always use a pair of forceps. Do not keep it out of water, and when you intend to cut a piece off a stick of phosphorus, place this in a basin with water and cut it under water. In experiments where carbondisulphide is used, be careful that the main supply bottle is kept at a distance from the phosphorus.

At times, in Experiment 10, the phosphorus reignites on the top of the tube on the removal of the cork; should it do this, cork the tube again and keep for a day or two longer. Or, if wished, a current of carbon dioxide may be passed down the tube, until the whole of the phosphorus vapor is displaced. The carbon disulphide may then be poured in safely.

In the preparation of phosphine, Experiment 11, the coal gas is passed in, in order to expel any air, as otherwise the phosphine would take fire within the flask and possibly burst it. Remember that, if any air remains with the coal gas, the phosphine may explode the mixture, and so cause considerable damage by scattering the molten phosphorus. This experiment is given more for the purpose of serving as an illustration than with the expectation that the inexperienced student is going to perform it. Should, however, the student desire to perform it, it would, according to the instructor's opinion, be safer to displace the air with carbon dioxide than with coal gas.

At the close of the experiment, allow the liquid in the flask to cool until water is drawn up into it from the trough. Pull out the cork, holding the flask in an old cloth, as the gas within the flask will take fire; have in readiness, therefore, a jug of cold water, with which at once fill the flask to the brim.

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## ARSENIC.

*Symbol As. Atomic weight 74.9. Density 149.8. Valence III and V. Molecular weight 299.6. One liter of arsenic vapor weighs 13.42 grams (149.8 criths).*

**68. History.**—This element is often classed among the metals, because it has a metallic luster and the property of conducting electricity; but, as it is not capable of forming a base with oxygen, and as the chemical character and composition of its compounds connect it closely with phosphorus, it certainly appears justifiable to consider it as a metalloid.

Sulphides of arsenic have been known for about 2,000 years; Aristotle and Dioscorides mention them. Pure arsenic was first obtained by Schroeder in 1694, but was more minutely examined by Brandt in 1733.

**69. Occurrence.**—Though closely resembling phosphorus in its chemical character and in the composition of its compounds, yet in its mode of occurrence in nature, arsenic more closely resembles sulphur. It is occasionally found in the uncombined state (native arsenic), but far more abundantly in combination with various metals, forming *arsenides*, which frequently accompany the sulphides of the same metals. The following are some of the chief ***arsenides*** and *arsenic sulphides* found in the mineral kingdom:

| | |
|---|---|
| Kupfernickel | $NiAs$ |
| Arsenical nickel | $NiAs_2$ |
| Tin-white cobalt | $CoAs_2$ |
| Arsenical iron | $Fe_2As_3$ |
| Mispickel | $FeS_2FeAs_2$ |
| Cobalt glance | $CoS_2CoAs_2$ |
| Nickel glance | $NiS_2NiAs_2$ |

But arsenic also occurs, like the metals, in combination with sulphur; thus, we have *red orpiment*, or ***realgar*** $As_2S_2$, and *yellow orpiment* $As_2S_3$. Sulphides of arsenic are also found in combination with other sulphides; thus, ***proustite*** $3Ag_2SAs_2S_3$ is a compound of the sulphides of silver and arsenic; *tennantite* contains sulphide of arsenic combined with sulphides of iron and copper; and ***gray copper ore*** is composed of sulphide of arsenic with the sulphides of copper,

silver, zinc, iron, and antimony. In an oxidized form, arsenic is found in *condurrite*, which contains arsenious anhydrite $As_4O_6$ and cuprous oxide. *Cobalt bloom* consists of cobalt arsenate $Co(AsO_4)_2$.

Arsenical pyrites is one of the principal sources of arsenic and its compounds, but a considerable quantity of it is also obtained in the form of arsenious oxide as a secondary product in the working of certain ores, especially those of copper, tin, cobalt, and nickel.

**70. Preparation.**—From arsenical pyrites, or mispickel, arsenic is obtained by heating it in earthen retorts. The arsenic, being volatile, sublimes and condenses in the cooler portions of the retort, towards its mouth. In certain districts, arsenic is obtained by reducing its oxide with charcoal—a method by which it is obtained in a much purer form.

**71. Properties.**—Arsenic presents the appearance of a dark, steel-gray, brittle solid, possessing a distinctly metallic luster, and having a specific gravity of 5.6 to 5.9. It occurs in two allotropic modifications, as, besides the steel-gray variety, which crystallizes in rhombohedrons and possesses the above mentioned specific gravity, an amorphous, black, vitreous variety, of specific gravity 4.71, exists, which at 360° passes into the crystalline variety with considerable evolution of heat. Arsenic is volatile in closed vessels at 500°; its vapor is yellow and possesses a peculiar odor, resembling that of garlic.

In the air, arsenic gradually oxidizes at ordinary temperatures, and, at a red heat, it burns with a bluish-white flame, producing arsenious oxide. Arsenic and all its compounds are active poisons.

Pure arsenic does not produce symptoms of poisoning till a considerable period after its administration, being probably first oxidized in the stomach and the intestines, and thus converted into arsenious acid. In the arts it is used in pyrotechny, in the manufacture of shot, insect powder, etc.

## ARSENIC AND HYDROGEN.

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### HYDROGEN ARSENIDE, OR ARSINE.

*Formula $AsH_3$. Molecular weight 77.9. One liter of arsine weighs 3.48 grams (39 criths).*

**72. History.**—Arsine, or, according to some authors, *arseneted hydrogen*, is the only compound of arsenic and hydrogen whose existence has been satisfactorily established. It was discovered by Scheele in 1775.

**73. Preparation.**—Arsine is prepared by the action of sulphuric acid, diluted with three parts of water, upon zinc arsenide, which is obtained by heating equal weights of zinc and arsenic in earthen retorts:

$$\underset{\text{zinc arsenide}}{Zn_3As_2} + \underset{\text{sulphuric acid}}{3H_2SO_4} = \underset{\text{arsine}}{2AsH_3} + \underset{\text{zinc sulphate}}{3ZnSO_4}$$

The gas is so poisonous in its character that its preparation in the pure state is always attended with a certain amount of danger.

**74. Properties.**—Arsine is a poisonous, colorless gas, with a sickly, alliaceous odor, and has a specific gravity of 2.7. It may be liquefied at $-55°$ and solidified at $-113°$. It is soluble in five times its volume of water. It takes fire readily in the air, burning with a bluish-white flame and evolving white fumes of arsenious oxide. If a cold surface of porcelain is held in this flame, metallic arsenic is deposited on it as a dark stain, or *tache*. Arsine is readily decomposed when the tube through which it is passing is heated to redness, a dark mirror-like ring of metallic arsenic being formed just beyond the heated spot. The gas is also decomposed when passed into a solution of silver nitrate, forming arsenious acid and precipitating metallic silver.

EXPERIMENT 14.—The chief interest attaching to this gas depends on the circumstance that its production allows the detection of very

minute quantities of arsenic in cases of poisoning. The application of one of these tests, known as *Marsh's test*, is also the safest method of preparing arsine in order to study its properties, for it is obtained so largely diluted with free hydrogen that it ceases to be *very* dangerous.

This test for arsenic depends on the production of arsine whenever arsenic is present in a soluble form in a solution in which hydrogen is evolved. A convenient form of *Marsh's apparatus*, largely and successfully employed by the most prominent chemists in this country, is shown in Fig. 18. It consists of a three-necked Woulff's bottle $A$,

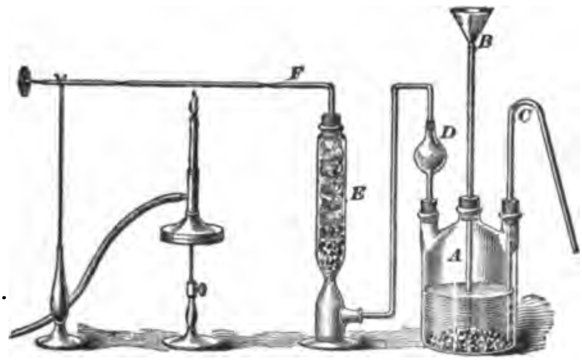


FIG. 18.

through the middle tubulure of which a funnel $B$ passes for the supply of liquid, while one of the side openings has a siphon tube $C$ for withdrawing the exhausted acid, and the other tubulure has a delivery tube with a bulb $D$. This bulb is filled with cotton, to retain any impurities that might be mechanically carried over by the gas. Attached to this leading tube is a jar $E$ filled with potassium hydroxide and calcium chloride. The object of this mixture in this jar is to purify the evolved gas, which then passes through another leading tube $F$, made of hard glass and drawn at intervals, as shown in the cut.

Small pieces of pure zinc are first placed in the Woulff's bottle, to which is added pure sulphuric acid, previously diluted with 3 parts of distilled water and thoroughly cooled (so as to have normal temperature). After allowing sufficient time for the air to be expelled from the apparatus, the leading tube $F$ is heated to dull redness by a Bunsen burner. If no dark deposit appears beyond the flame in 15 minutes, the materials employed may be considered chemically pure. The liquid suspected to contain arsenic is then added through the funnel tube. If arsenic should be present, the flame of hydrogen burning at the end of the tube will, often in a few seconds, change its color, becoming whitish, and will deposit a dark-brown metallic spot on a porcelain plate pressed down upon it. If the tube is again heated, the

arsine will be decomposed, and the arsenic be deposited as a dark metallic ring. According to Wormley, $\frac{1}{100000}$ of a grain of arsenious oxide in 100 grains of the solution may be detected by this test.*

**75. Precaution.**—Never forget that arsine is one of the most active poisons with which we are acquainted. It should, therefore, be experimented on only with the very greatest care.

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## OXIDES AND ACIDS OF ARSENIC.

**76.** The oxides of arsenic, with their corresponding acids, are the following:

| *Oxides.* | | *Acids.* | |
|---|---|---|---|
| Arsenious oxide | $As_2O_3$ | Arsenious acid | $H_3AsO_3$ |
| Arsenic oxide | $As_2O_5$ | Arsenic acid | $H_3AsO_4$ |

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### ARSENIOUS OXIDE.

*Formula $As_2O_3$. Molecular weight 197.68.*

**77. Occurrence and Preparation.**—Arsenious oxide occurs native as the mineral arsenolite. Arsenious oxide is manufactured by roasting certain arsenical ores—mostly arsenical pyrites found in the mines of Silesia in Germany—in muffles or ovens through which air is allowed to pass, when the arsenic contained in the ores is converted into $As_2O_3$ and the sulphur, which is also present in the pyrites, into $SO_2$. These gases are conducted into large chambers in which the $As_2O_3$ is deposited as a very fine powder, or, more properly speaking, dust. The fine dust thus obtained is purified by resublimation.

The removal of the arsenious oxide from the condensing chambers is a very unwholesome operation, owing to its dusty and extremely poisonous character.

**78. Properties.**—Arsenious oxide occurs in two distinct modifications. When the arsenious-oxide vapor is condensed

* Some other tests employed for the detection of arsenic, used by physicians and coroners, will be given in *Qualitative Analysis*.

at a temperature of 400°, it forms a transparent vitreous mass of a specific gravity of 3.738, which, when deposited slowly at a temperature slightly less elevated, crystallizes in right rhombic prisms. The second variety is obtained in brilliant transparent octahedral crystals of specific gravity 3.689, either by condensing the vapor at 200°, or by cooling a saturated aqueous solution of arsenious oxide of the first variety.

The first mentioned, or vitreous, variety passes gradually at ordinary temperatures, rapidly at about 100°, into the second variety, forming a white, opaque mass resembling porcelain, commonly known as *white arsenic.*

When the vitreous variety is dissolved to saturation in hot hydrochloric acid and left to cool slowly, it crystallizes in octahedrons, the formation of each crystal being accompanied by a flash of light.

Arsenious oxide volatilizes at 218°, yielding a vapor with a density of about 198 instead of about 99, which indicates that the vitreous modification formed at high temperatures has the molecular formula $As_4O_6$. Owing to this fact, in most textbooks of chemistry the formula of arsenious oxide is given as $As_4O_6$.

Both varieties of arsenious oxide are sparingly soluble in water, but are more soluble in alkaline solutions and in hydrochloric acid.

The arsenious oxide sold in stores as white arsenic is a fine, white powder, dangerously resembling flour in appearance, but, being so much heavier, mistakes that so often occur are hardly pardonable, and with a little care should certainly be entirely avoided.

This common poison, however, may fortunately be easily recognized by its weight, and by sprinkling it upon a red-hot coal, when a strong odor of garlic is perceptible, due to the reduction of $As_2O_3$ by the heated carbon, the vapor of arsenious oxide being itself inodorous. The slight solubility of arsenious oxide in water is rather unfavorable to its action as a poison; for, when thrown into ordinary liquids, it is dissolved in very small quantities, the greater part of it collecting at the bottom of the vessel containing the liquid.

Even when taken into the stomach in a solid state, its want of solubility delays its operation sufficiently to give a better chance of antidotal treatment than in the case of most other common poisons. The best antidotes for arsenic are freshly prepared ferric or magnesic hydrate. The fact that arsenious oxide is almost tasteless, proves its comparative insolubility.

When thrown into water, white arsenic exhibits great repulsion for the particles of that liquid, and collects in a characteristic manner around little bubbles of air, forming small white globes, which are not wetted by the water. Even if stirred with water and allowed to remain in contact with it for some hours a pint of water would not take up more than 20 grains. If boiling water is poured on powdered white arsenic and allowed to remain with it till cold, it will dissolve about $\frac{1}{400}$ of its weight (22 grains in a pint).

Although so small a quantity as 1 or 2 decigrams of white arsenic has been known to prove fatal, the administration of gradually increasing doses will so inure the system to the poison that comparatively large quantities can be taken internally at frequent intervals. When administered in this manner, arsenious oxide appears to have a remarkable effect on the animal body.

Horse and cattle dealers occasionally employ it to improve the appearance of their stock, and in the Tyrol and Styria, Austria, it is frequently taken by men and women, perhaps not so much for the sake of the improvement in appearance, as for the fact that it has a certain stimulating effect upon the animal system, and enables these people, living in wild mountainous regions, to better endure the hardships of climate, and the climbing of mountains—often encumbered as these people are with great burdens. The continuance of the usage of white arsenic, like any other stimulant, however, creates a certain craving for this drug, and the doses of it have to be gradually increased. The serious consequences of this battle against nature never fail to appear, and the slow but steady depopulation of these mountain districts is a sad proof of this fact.

### ARSENIOUS ACID.

*Formula* $H_3AsO_3$. *Molecular weight 125.78.*

**79. Preparation and Properties.**—When arsenious oxide is dissolved in water, an acid, styptic liquid is obtained, which decomposes on evaporation.

This aqueous solution of arsenious oxide, when neutralized exactly with ammonia, yields, with silver nitrate, a yellow precipitate having the composition $Ag'_3AsO_3$; with cupric sulphate, a green precipitate having the composition $Cu''HAsO_3$; and with magnesium sulphate, a white precipitate having the composition $Mg''HAsO_3$. These precipitates show that the arsenious acid from which these salts are obtained is tribasic, and must have the formula $H_3AsO_3$. The fact that arsenious acid does not destroy alkaline reactions of alkalies nor decompose alkaline carbonates, unless heat is applied, proves it to be a feeble acid.

The arsenites, as a rule, are much more stable than arsenious acid, and include both ortho-arsenites and meta-arsenites.

The arsenites of potassium and sodium are sometimes employed as a sheep-dipping composition, oftener in Australia than in the United States; and an arsenical soap, composed of potassium arsenite, soap, and camphor, is used by naturalists to preserve the skin of animals. Sodium arsenite is also said to be occasionally used for preventing incrustations in steam boilers, being prepared for that purpose by dissolving 1 molecule of arsenious oxide and 2 molecules of sodium carbonate.

*Scheele's green* $CuHAsO_3$, an arsenite of copper, is obtained by dissolving arsenious oxide in a solution of potassium carbonate and decomposing the arsenite of potassium thus obtained by adding sulphate of copper, when the arsenite of copper is precipitated. This poisonous color is very often used in the manufacture of wall paper, and is rather injurious to the health of the occupants of a room papered with this bright-green wall paper. The arsenite of copper, being only fixed with glue or some other kind of paste, rubs off the paper, and is diffused through the air of the room as a very

fine dust, a small proportion of it being consequently inhaled with each breath; and a continuous occupancy of a room decorated in this manner will soon cause headache and even more serious illness.

The presence of arsenite of copper in a sample of green wall paper is easily proved by soaking such sample in a little ammonia, which dissolves the arsenite of copper, forming a blue liquid. The presence of arsenic in this blue liquid may be proved by acidifying it with a little chemically pure hydrochloric acid, and boiling it with a couple of strips of pure copper. These strips of copper will, on boiling, become covered with a steel-gray coating of arsenite of copper. On washing the copper, drying it on filter paper, and heating it in a test tube, the arsenic will be converted into arsenious oxide, which will be deposited in octahedral crystals on the cool parts of the tube.

As a precautionary measure, some of the ammonia, hydrochloric acid, and copper should be tested first, without the paper, in exactly the same way; so as to avoid mistakes, and to be positive that none of these contain arsenic, and that in the test the arsenic is actually derived from the paper and *not* from any of the reagents employed.

The really effective and beautiful green color of arsenite of copper leads often to its employment as a dye of muslins, calicoes, feathers, and, incredible as it may seem, even for the coloring of candies, etc.

*Emerald green* is a combination of arsenite and acetate of copper, obtained by mixing hot solutions of equal weights of arsenious oxide and acetate of copper.

Fowler's solution, a solution of potassium arsenite, is frequently used in medicine.

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### ARSENIC OXIDE.

*Formula* $As_2O_5$. *Molecular weight 229.6.*

**80. Preparation and Properties.**—Arsenic oxide, which may be obtained by heating arsenic acid to dull redness, is an opaque, amorphous, white mass, which deliquesces

in the air and dissolves rather reluctantly in water to form arsenic acid. Arsenic oxide fuses at a bright-red heat, and decomposes into arsenious oxide and oxygen.

---

### ARSENIC ACID.

*Formula* $H_3AsO_4$. *Molecular weight 141.74.*

**81. Preparation and Properties.**—Arsenic acid is produced by oxidizing either arsenious oxide or arsenious acid with three-fourths of its weight of nitric acid, specific gravity 1.35, when it dissolves with the evolution of considerable heat and red fumes of nitrous oxide

$$\underset{\text{arsenious oxide}}{2As_2O_3} + \underset{\text{nitric acid}}{4HNO_3} + \underset{\text{water}}{4H_2O} = \underset{\text{nitrous oxide}}{2N_2O_3} + \underset{\text{arsenic acid}}{4H_3AsO_4}$$

and evaporating it to a syrupy liquid. On standing, long rhomboidal crystals separate, which contain water of crystallization and are deliquescent. At 100° this water is expelled, and needle-shaped crystals of the $H_3AsO_4$ are produced. Its aqueous solution is strongly acid. On heating arsenic acid to 150°, di- or pyro-arsenic acid $H_4As_2O_7$ results:

$$2H_3AsO_4 - H_2O = H_4As_2O_7$$

Between 200° and 206° another quantity of water is driven off, and on cooling there remains a pasty, pearly mass, which is meta-arsenic acid $HAsO_3$:

$$H_3AsO_4 - H_2O = HAsO_3$$

Arsenic acid and its salts are poisonous, but to a less extent than any of the arsenious compounds.

**82.** Arsenic acid has acquired considerable importance in the last years, having been successfully used as a substitute for the much more expensive tartaric acid used in calico printing, and, also, having furnished, by its action on aniline, the beautiful dye known as *magenta*.

**83.** Among the salts of arsenic acid (arsenates), the common *arsenate of soda* $Na_2HAsO_4,7Aq$ is extensively used by calico printers, as a substitute for the dung baths formerly

employed; since, like the common phosphate of soda, it possesses the feebly alkaline properties required in that particular part of the process. It is manufactured by combining arsenious oxide with soda, and heating the resulting arsenite with sodium nitrate, from which it acquires oxygen, becoming converted into sodium arsenate.

Calcium arsenate $2CaHAsO_4,7H_2O$ has been found in crystalline crusts at Joachimsthal, in Saxony, Germany. Arseniosiderite and xanthosiderite are calcium ferric arsenates.

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## ARSENIC AND CHLORINE.

**84. Arsenious chloride** $AsCl_3$ is the only positively known chloride of arsenic. It is produced, with the emission of heat and light, when powdered arsenic is thrown into chlorine gas. It is prepared by distilling a mixture of 1 part of arsenic and 6 parts of corrosive sublimate; or by distilling $As_2O_3$ with strong hydrochloric acid.

Arsenious chloride is a colorless, oily, and very dense liquid, which boils at 134°. Its density at 0° is 2.05. It gives off white fumes in the air and is very poisonous.

An excess of water decomposes it at once into hydrochloric acid and arsenious oxide, which, being but slightly soluble, is precipitated:

$$4AsCl_3 + 6H_2O = 2As_2O_3 + 12HCl$$

**85. Arsenious bromide** and **iodide** are formed in an analogous manner. **Arsenious fluoride** $AsF_3$ is also known, and may be prepared by distilling a mixture of arsenious oxide, fluorspar, and sulphuric acid in a lead retort. It is obtained as a colorless liquid.

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## ARSENIC AND SULPHUR.

**86.** Three sulphides of arsenic are known:

| | |
|---|---|
| Arsenic disulphide, or realgar, | $As_2S_2$ |
| Arsenic trisulphide, or orpiment, | $As_2S_3$ |
| Arsenic pentasulphide | $As_2S_5$ |

**87. Arsenic disulphide** $As_2S_2$ occurs in nature in the form of transparent red crystals, which belong to the type of the oblique rhombic prism. It is formed artificially by heating arsenic acid with the proper proportion of sulphur. It is fusible and may be crystallized by slow cooling. When strongly heated in a closed vessel, it boils and distils without alteration; but, when heated in the air, it burns into arsenious and sulphurous oxides. The alkaline sulphides and ammonium sulphide dissolve realgar, leaving a brown powder, which is considered to be a subsulphide of arsenic. A boiling solution of potassium hydrate also dissolves realgar, forming a mixture of potassium arsenite and sulpharsenite; the latter is a soluble compound of arsenic trisulphide and potassium sulphide.

**88. Arsenic trisulphide,** or **orpiment,** $As_2S_3$ is found native in yellow prismatic crystals. It may be obtained by fusing together arsenic and sulphur in the proper proportion, or arsenious oxide and sulphur; in the latter case, sulphurous oxide is disengaged and arsenic trisulphide sublimes. Thus prepared, orpiment occurs as crystalline masses of a yellow or, more correctly, yellow-orange color, and is of a pearly aspect. It is fusible and volatile.

**89. Arsenic pentasulphide** $As_2S_5$ is precipitated when an excess of hydrogen sulphide is passed into a solution of arsenic acid heated to 70°, or, still better, when an acid is added to a solution of sodium sulpharsenate. It is a lemon-yellow powder, which is insoluble in water, and which may be fused and distilled without alteration.

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## CARBON.

*Symbol C. Atomic weight 11.97.* Valence II (?) and IV.*

**90. Occurrence.**—Carbon is especially remarkable for

* As carbon is a non-volatile substance, its density and molecular weight have not been determined.

its uniform presence in all organic substances; and the ordinary laboratory test by which the chemist decides whether a substance he is examining or analyzing is of organic origin or not, consists in heating it with limited access of air, and observing whether any blackening from separation of carbon (carbonization) ensues.

Carbon occurs native in two allotropic forms, known, respectively, as the *diamond* and *graphite*. It also occurs, more or less impure, in the various forms of mineral coal. In combination with hydrogen, it is met in bitumen and petroleum. It exists in the air, and, combined with oxygen and calcium, it forms limestone, one of the most abundant rock formations.

**91. Preparation.**—By heating wood, coal, or bones in a closed vessel, carbon in an impure state may be readily

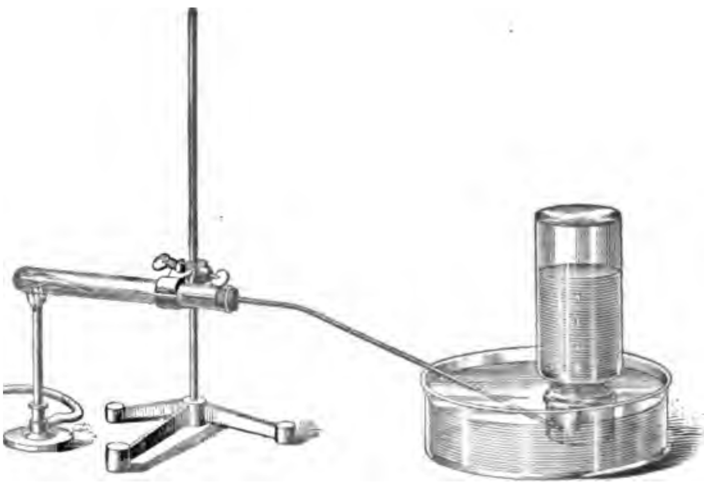

FIG. 14.

obtained. Water and volatile compounds of carbon with hydrogen and oxygen are driven off; the excess of carbon remains, together with the non-combustible portions of the wood or other body.

**Experiment 15.**—Fit up an apparatus as shown in Fig. 14, consisting of a combustion tube connected by a cork to a leading tube, which terminates in the pneumatic trough, and place some pieces of dry wood in the tube. Fix the tube in the retort stand with its mouth slightly lower than the other end, in order to prevent any of the liquid that distils from running back on the hot part of the glass tube. Place a bottle for the collection of the gas, and apply heat to the combustion tube; some water and tarry liquid condense in the cooler part of the tube and an inflammable gas passes over into the jar. When the action ceases, a black mass remains of approximately the same shape as the original wood, still retaining the grain and marks of the woody structure. This body is *charcoal.*

This process of heating a body and causing its decomposition, in part, into gaseous and liquid products, which are collected, is termed *destructive distillation.*

**92. Properties.**—I. *As Diamond.*—The form of carbon known as *diamond* is a brilliant, transparent, and usually colorless solid, having a specific gravity of 3.5, and crystallizing in forms belonging to the isometric system, the faces being often rounded, as shown in Fig. 15. Carbon in this form conducts neither heat nor electricity, but possesses a very high refractive and dispersive power. It is the hardest matter known, scratching or cutting all other bodies. Small crystals set in proper holders are used for cutting glass. The diamond occurs in India, Borneo, South Africa, and other localities. It is cut for a gem into forms having relations to its direction of cleavage—known as the brilliant, the rose, and the table—by means of diamond dust. This diamond dust is usually obtained from a dark amorphous diamond (carbonado) found at Bahia, in the Brazils.

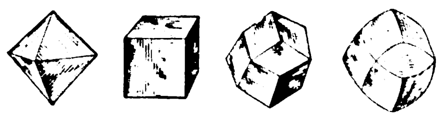

Fig. 15.

A genuine diamond may be known by its combining the three qualities of extreme hardness (enabling it to scratch hardened steel), high specific gravity, and insolubility in hydrofluoric acid.

Artificial diamonds have been made by dissolving amorphous carbon in molten iron at nearly 3,000°, and suddenly cooling the metal by pouring it into melted lead. In this way only the surface of the globules of iron is immediately solidified. The interior expands as it cools and creates that pressure on the carbon it contains, which appears to be essential to the formation of diamond. By dissolving the iron in acids, the diamonds are left. They are, however, of no mercantile value, being only very small fragments; besides they are, so far as brilliancy is concerned, not comparable with the natural product.

Apart from its value, caused by its rarity and beauty, the diamond possesses a certain interest from a chemical point of view, having perplexed philosophers up to the middle of the last century, notwithstanding the simplicity of the experiments required to demonstrate its true nature. The first idea of it appears to have been obtained by Newton, when he perceived its great refracting power, from which he inferred that, like other bodies possessing this property in a high degree, it would prove to be combustible. When the prediction was verified, the burning of diamonds was considered a marvelous experiment, though apparently no accurate observations were made until 1772, when Lavoisier ascertained, by burning diamonds suspended in the focus of a burning glass in a confined portion of oxygen, that they were entirely converted into carbonic-acid gas.

On exposing the diamonds to the intense heat of the voltaic arc, in a vessel exhausted of air, a black coke-like mass results, which closely resembles graphite in all its properties.

II. *As Graphite.*—The second form of carbon, known as *graphite*, differs from the diamond in almost every characteristic. It occurs in compact masses, which appear to be more or less crystalline, the more perfect crystals appearing as hexagonal plates, Fig. 16—a crystalline shape, as the student will notice, totally different from that of the diamond. Graphite is a leaden-gray solid with a semimetallic luster, and has consequently received the names

Fig. 16.

*plumbago* and *black lead.* It has a specific gravity of 2 to 2.2, and conducts heat and electricity readily. It is soluble in melted iron, from which it crystallizes on cooling.

Graphite occurs, foliated as well as massive, in metamorphic rocks in Siberia, Ceylon, England, and various places in the United States—as, for instance, in Sturbridge, Mass., Brandon, Vt., Wake, N. C., etc. It is purified by treating it with potassium chlorate and nitric acid, and is, after drying, condensed into a solid block by hydrostatic pressure. This method of purification is known as *Brodie's process.* The finer qualities of graphite, especially those coming from Siberia, are employed in the manufacture of black-lead pencils; the coarser qualities are used in the manufacture of crucibles, and, as it has a peculiar greasy feel, it is sometimes used for lessening the friction between two rubbing surfaces of various kinds of machinery.

III. *As Coal.*—The various substances classed under the name of coal are characterized by the presence of carbon as a predominent constituent, associated with varying quantities of oxygen, hydrogen, nitrogen, sulphur, etc. The purest variety of coal is known under the name of *anthracite*, which is an amorphous, black, hard, and somewhat lustrous body, rather hard to render combustible, and containing between 80 and 94 per cent. of carbon, with specific gravity varying from 1.3 to 1.7.

From this there is a regular gradation through *cannel* and *bituminous coals* of all varieties to *lignite*, or *brown coal*, which is sometimes only scarcely altered wood. All coal is derived from primitive vegetation, changed and consolidated by heat and pressure. Anthracite coals are found where the strata have been most exposed to heat or disturbed by volcanic motions; bituminous where the strata are nearly or quite horizontal; while brown coal is much more recent in age, being generally tertiary.

**93.** Several varieties of carbon, so called *pseudocarbons*, obtained by artificial processes, are largely employed in the arts.

The most important of these are *lampblack*, *wood charcoal*, and *animal charcoal*.

**Lampblack** approaches more nearly in composition to pure carbon than either of the others; it is the soot obtained from imperfect combustion of resinous and tarry matter—a source from which it derives the small quantities of resin, nitrogen, and traces of sulphur it contains. It is largely used as an ingredient of pigment, printing ink, and blacking, but perhaps more on account of its black color than its chemical properties.

**Diamond black** is an extremely pure quality of lampblack, obtained by the imperfect combustion of the natural hydrocarbon gas of the Ohio petroleum regions. **Spanish black** is charcoal made from cork.

**Wood charcoal** represents more features that arrest the attention of the chemist than any other pseudocarbon mentioned, on account of its various properties.

Its preparation on a small scale has been already demonstrated by Experiment 15. If it is used for fuel it is generally prepared by a process in which the heat developed by the combustion of a portion of the wood is made to effect the charring of the rest.

With this end in view, sticks of wood are built up into a

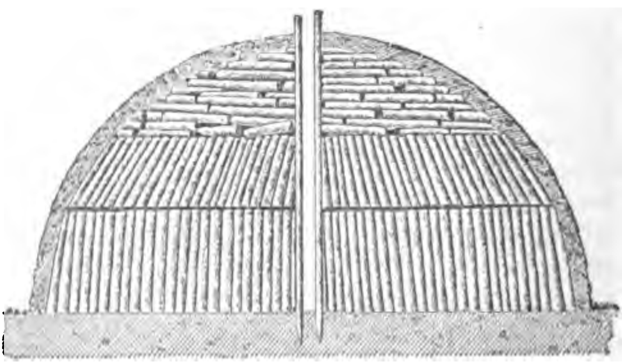

FIG. 17.

heap, as shown in Fig. 17, around stakes driven into the ground, a passage being left, so that the heap may be kindled

in the center. This heap of wood, generally from 30 to 50 feet in diameter, is closely covered with turf and sand, except for a few inches around the base, where it is left uncovered, for the purpose of allowing the escape of the vapor of water expelled in the beginning of the process. When the heap has been kindled in the center, the passage left for this purpose is carefully closed up. After the combustion has proceeded for some time, and it is estimated that the wood has been perfectly dried by the heat evolved, the open space at the base is also closed with sand and turf, and the heap left to smolder for three or four weeks, when the wood is perfectly carbonized. Upon an average, 100 per cent. of wood gives 22 per cent. of charcoal.

A far more economical process for preparing charcoal from wood consists in heating it in iron cylinders—a bluish-black, porous substance having a specific gravity of 1.7 and retaining minutely the form of the original wood being thus obtained.

**Animal charcoal,** or **bone black,** obtained by igniting bones in closed vessels, is also a black, porous mass, containing, upon an average, 90 per cent. of calcium phosphate.

**94.** In all its forms, carbon is infusible and non-volatile. This infusibility of charcoal accounts for its great porosity, on which some of its most remarkable and useful properties depend. The application of charcoal for the purpose of *sweetening* meat and fish in a state of incipient putrefaction has been practiced for many years, and more recently charcoal has been employed for *deodorizing* all kinds of putrefying and offensive animal and vegetable matter.

This property of charcoal depends on its power of absorbing into its pores very considerable quantities of gases, especially those that possess a great attraction for water and are easily absorbed by it. One cubic inch of charcoal is, for instance, capable of absorbing 100 cubic inches of ammonia and 50 cubic inches of hydrogen sulphide, both of which are conspicuous among the offensive results of putrefaction. This condensation of gases by charcoal is, however, a mechanical effect, and does not involve a chemical combination

of the charcoal with the gas; it is exhibited most powerfully by charcoal that has been recently heated to redness in a closed vessel, and cooled out of contact with the air by being plunged under mercury. Eventually, the offensive gases absorbed by the charcoal are chemically acted on by the oxygen of the air in its pores. One cubic inch of wood charcoal absorbs nearly 10 cubic inches of oxygen; and, when the charcoal containing this gas thus condensed is presented to another gas capable of undergoing oxidation, this latter gas is oxidized and converted into inodorous products. For instance, charcoal, on being exposed to the action of air containing hydrogen sulphide $H_2S$, condenses within its pores not only this gas, but also atmospheric oxygen, which slowly converts the $H_2S$ into sulphuric acid $H_2SO_4$. The presence of so much air in charcoal renders it, like wood, apparently lighter than water; and though the specific gravity varies from 1.4 to 1.9, a solid piece of charcoal always floats on water, while finely powdered charcoal descends to the bottom of the vessel.

**95.** All the gases evolved in putrefaction are more or less poisonous, and, as charcoal is capable of removing them, it has acquired a certain amount of practical importance, and is applied in a great number of cases.

To prevent the evolving of obnoxious fumes, coarsely powdered charcoal is thickly strewn over the matter from which the *effluvium* proceeds; or the charcoal is exposed in shallow trays to the air to be sweetened, as in the wards of hospitals, etc. It has even been placed in a flat box of wire gauze to be fixed as a ventilator before a window through which contaminated air might have access; and respirators constructed on the same principle have been found to give satisfactory protection against poisonous gases and vapors in certain chemical works.

**96.** Water is often filtered through charcoal, in order to free it from any putrescent organic matter it may contain, the power of absorption, which charcoal possesses, not being

confined to gases alone; many solid and liquid substances are capable of being removed by this agent from their solution in water.

This fact is most readily traced in the case of substances that impart a color to the solution, such color being frequently removed by the absorbing power of the charcoal employed.

EXPERIMENT 16.—Take either some port wine, dark-brown syrup, or beer; shake a little of it up in a test tube with finely powdered charcoal; allow the charcoal to subside, and then filter off; note that the filtrate is greatly decolorized.

**97.** Comparing the decolorizing power of vegetable charcoal with that of animal charcoal, or, as it is more commonly known, bone black, the power of the former appears to be rather feeble.

Bone black is obtained, as has been previously stated, by heating bones in vessels from which the air is excluded. The composition of bones consists of about one-third of animal and two-thirds of mineral substances, the latter including calcium phosphate (which amounts to more than half of the weight of the bone) and a little calcium carbonate. When bone is heated, as in a retort, so that air is not allowed to have free access to it, the animal matter undergoes destructive distillation, its elements—carbon, hydrogen, nitrogen, and oxygen—assuming other forms, the greater part of the last three elements mentioned, together with a portion of the carbon, escaping in different gaseous and vaporous products, while a considerable proportion of the carbon remains behind, intimately mixed with the earthy ingredients of the bone, and constituting the substance known as animal charcoal.

**98.** The existing difference between the products of the destructive distillation of bones and wood, justly deserve some notice at this place.

If a piece of bone is heated in a glass tube, as shown in Fig. 14, the vapors evolved are found to be alkaline in their reaction to test paper, while the vapor produced by the

distillation of wood will produce an acid reaction. This difference of reaction may be traced back mainly to the presence of nitrogen in bone; wood, on the other hand, being nearly free of this element. It will be found to hold good, as a general rule, that the results of the destructive distillation of animal or vegetable matter containing a considerable amount of nitrogen are alkaline, owing to the presence of ammonia and other similar compounds, while those furnished by non-nitrogenized substances possess an acid character. The peculiar odor emitted by heated bones is characteristic, and affords a rough test by which to distinguish between nitrogenized and non-nitrogenized bodies.

An examination of the charred mass remaining as the final result of the action of heat on bone, shows it to contain much less carbon than that furnished by wood, for bone charcoal contains nearly nine-tenths of its weight of phosphate of calcium. The consequence of the presence of so large an amount of earthy matter must be to extend the particles of carbon over a larger space, and thus to expose a greater surface for the adhesion of coloring matters. This fact may, at least partly, help to explain the very great superiority of bone black to wood charcoal as a decolorizing agent, and this explanation derives support from the circumstance that, when animal charcoal is deprived of its earthy matter by washing with hydrochloric acid, its decolorizing power becomes largely reduced.

The application of animal charcoal as a decolorizing agent is not confined solely to the laboratory, but finds wide employment in various manufacturing processes, such as sugar refining, in the distillation of spirits, etc.

**99.** One of the most remarkable features of carbon is its indisposition to enter directly into combination with other elements. It appears, in fact, as if this element was incapable of uniting with any other element at ordinary temperatures; and this circumstance is turned to useful account, as, for instance, when the ends of wooden stakes are charred before being driven into the earth, where the

action of atmospheric oxygen, which, in the presence of moisture, would be very active in effecting the decay of the wood, is resisted by the charcoal into which the external layer has been converted. Charred piles driven by the Britons to prevent Julius Cæsar from crossing the Thames, and wheat charred nearly 2,000 years ago at Herculaneum, are yet found unchanged. The employment of black lead to protect metallic surfaces from rust is another application of the same principle. At a high temperature, however, carbon combines readily with oxygen, sulphur, and with some of the metals, and, at a very high temperature, even with hydrogen and nitrogen. The tendency of carbon to combine with oxygen under the influence of heat is shown when a piece of charcoal is strongly heated at one point, when the carbon at this point at once combines with the oxygen of the surrounding air, forming carbon dioxide, and the heat developed by this combustion raises the neighboring particles of carbon to the temperature at which this element unites with oxygen; and thus the combustion is gradually spread throughout the mass, which is ultimately converted entirely into carbon dioxide, nothing remaining but the white ash composed of the mineral substances derived from the wood employed for preparing the charcoal. It is worthy of note that, if charcoal had been a better conductor of heat, it would not have been so easily kindled, since the heat applied to any point of the mass would have been rapidly diffused over its whole bulk, and this point could not have attained the high temperature requisite for its ignition, until the whole mass had been heated nearly to the same degree; this is actually found to be the case in charcoal that has been very strongly heated (out of contact with air), when its conducting power is greatly improved, and it kindles with great difficulty. The ignition temperature of carbon in the shape of charcoal appears to be about 400°. The calorific value of wood charcoal is represented by the number 8,080; that is, 1 gram of carbon, when burned so as to form carbon dioxide, is capable of raising 8,080 grams of water from 0° to 1°.

A given weight of charcoal will produce twice as much available heat as an equal weight of wood, since the former contains more actual fuel and less oxygen, and much of the heat evolved by the wood is absorbed or rendered latent in the steam and other vapors, which are produced by the action of the heat upon it.

**100.** The very striking difference in the properties exhibited by diamond, graphite, and charcoal, leads to the belief that they consist of dissimilar carbon molecules. The investigation of the specific heats and other physical constants of these three varieties indicates that the diamond molecule contains more atoms than the graphite molecule, and that the charcoal molecule is still less complex.

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## CARBON AND HYDROGEN.

**101.** The compounds of carbon and hydrogen—called *hydrocarbons*—are very numerous, and, as most of them are distinctly of organic origin, their study is usually undertaken as a part of organic rather than inorganic chemistry.

Only three of them, therefore, will be described here:

| | |
|---|---|
| Hydrogen carbide | $H_4C$ |
| Hydrogen dicarbide | $H_4C_2$ |
| Dihydrogen dicarbide | $H_2C_2$ |

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### HYDROGEN CARBIDE, OR METHANE.

*Formula $H_4C$. Density 7.985. Specific gravity .551. Molecular weight 15.97. One liter of methane weighs .715 gram (7.985 criths).*

**102. Occurrence.**—Methane occurs free in nature, being evolved during the decomposition of dead vegetable matter confined under water; hence, it is found in marshy districts, and has thus received its common name of *marsh gas.* On watching stagnant water, bubbles of the gas may

be seen to arise, and may be collected by inverting a jar, filled with water, in the pool. During the changes that have occurred while coal has been forming from vegetable growths, marsh gas has also been evolved and has remained imprisoned within cavities of the coal itself. As the coal is removed by the miner, the gas escapes from these cavities into the mine, and, mixing with the air forms the explosive mixture that has been the cause of so many colliery accidents. The collier knows this gas as *firedamp*. It often occurs largely in the vicinity of salt wells, as in Kanawha, West Virginia. It constitutes nearly the whole of the so called natural gas, which has come so extensively into use in some cities for purposes of lighting and heating.

**103. Preparation.**—Marsh gas is obtained artificially by the following process:

EXPERIMENT 17.—Ten grams of dried sodium acetate are finely powdered and mixed, in a mortar, with 10 grams of caustic soda. The mixture is heated in a test tube (a copper test tube is preferable, as the alkali corrodes the glass) and the gas collected over water, as shown in Fig. 14.

The formation of marsh gas will be evident from the following equation:

$$\underset{\text{sodium acetate}}{NaC_2H_3O_2} + \underset{\text{caustic soda}}{NaOH} = \underset{\text{sodium carbonate}}{Na_2CO_3} + \underset{\text{marsh gas}}{H_4C}$$

**104. Properties.**—Marsh gas is a light, colorless gas, and has therefore received the name of *light carbureted hydrogen*. It is odorless and tasteless, and is but slightly soluble in water. It is not a supporter of combustion, but burns with a non-luminous flame, resembling that of hydrogen, but slightly tinged with yellow. Marsh gas forms an explosive mixture with 2 volumes of oxygen, or 10 volumes of air, and is the cause of the serious mine explosions, which sometimes happen in the coal districts. Until recently, marsh gas was considered to be a permanent gas, but, in common with hydrogen and other gases, it has now been

liquefied. By the action of chlorine on marsh gas, its hydrogen is gradually replaced by chlorine, forming, successively, the compounds $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$, and $CCl_4$.

Marsh gas constitutes the first member of a homologous series of hydrocarbons known as the marsh-gas series, the successive members increasing uniformly by $CH_2$. They are all saturated substances, having the general formula $C_nH_{2n+2}$; that is, they contain twice as many atoms of hydrogen as of carbon, plus 2. They constitute the essential portion of the various native petroleums.

EXPERIMENT 18.—The lightness and inflammability of marsh gas may be shown by introducing a lighted taper into a jar of it, held mouth downwards. The gas will burn at the mouth of the jar, and the flame of the taper, as it is passed up into the jar filled with the gas, will be extinguished.

**105. Composition of Marsh Gas by Volume.**—The composition of this gas may be ascertained by exploding it with an excess of oxygen in the eudiometer. If 10 volumes of marsh gas are mixed with 25 volumes of oxygen, there will be found after explosion, at a temperature above 100°, 35 volumes of gas. On cooling to normal temperature, the gas contracts to 15 volumes; there must, consequently, have been present 20 volumes of water vapor. On introducing caustic potash, a further absorption of 10 volumes occurs, showing that 10 volumes of carbon dioxide have been formed. The residual 5 volumes of gas are found on examination to be oxygen. One volume, therefore, of this gas requires for its combustion 2 volumes of oxygen, and produces 1 volume of carbon dioxide and 2 volumes of water vapor.

Remembering that by Avogadro's law the molecular volume of all gases is equal, and that the molecule of hydrogen contains 2 atoms, then, as 2 volumes of the gas yield 2 volumes of carbon dioxide, or 1 molecule yields 1 molecule of carbon dioxide, 1 molecule of marsh gas contains 1 atom of carbon. Again, 2 volumes of marsh gas produce 4 volumes of water vapor; that is, 1 molecule of marsh gas yields 2 molecules of water; and, as each molecule of water contains

2 atoms of hydrogen, the molecule of marsh gas contains 4 atoms of hydrogen. The formula must consequently be $CH_4$.

**106. Composition by Weight.**—The composition by weight of marsh gas is ascertained by passing a known volume of the gas through a combustion tube containing red-hot copper oxide. Carbon dioxide and water are formed, and are absorbed in weighed tubes containing, respectively, calcium chloride, which absorbs the water, and caustic potash, by which the carbon dioxide is retained. The increase in weight gives the amounts of these two bodies formed from the marsh gas.

In an experiment, performed by the writer, a volume of $CH_4$, equivalent to 1,000 cubic centimeters at normal temperature and pressure, was passed over red-hot copper oxide; there were produced 1.611 grams of water and 1.965 grams of $CO_2$. From these data the composition of the gas was calculated in the following manner:

Weight of 1,000 cubic centimeters of marsh gas = .0896 × 7.98 (density) = .715 gram.

Weight of carbon $\dfrac{1.955 \times 12}{44} = .536$ gram.

Weight of hydrogen $\dfrac{1.611 \times 2}{18} = .179$ gram.

From these weights, the percentage composition—namely, 75 per cent. of carbon and 25 per cent. of hydrogen by weight—is readily obtained. Having these facts and employing formula **2**, Art. **82**, *Theoretical Chemistry*,

$$n = \frac{m\,x}{100\,a},$$

and substituting the proper value, we obtain,

for carbon, $\quad n = \dfrac{16 \times 75}{100 \times 12} = 1;$

for hydrogen, $\quad n = \dfrac{16 \times 25}{100 \times 1} = 4.$

Hence, the simplest formula of marsh gas must be, from this experiment, $CH_4$. Whether or not this is the true formula, may be determined by calculating the density from the molecular formula, $CH_4$.

$$\text{Density} = \frac{\text{molecular weight} = C = 12 + H_4 = 4 = 16}{2} = 8.$$

This number agrees closely with the density as determined by experiment; $CH_4$ is therefore the correct molecular formula of marsh gas.

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### HYDROGEN DICARBIDE, OR ETHYLENE.

*Formula $H_4C_2$. Density 13.97. Specific gravity .965. Molecular weight 27.94. One liter weighs 1.25 grams (13.97 criths).*

**107. History.**—Ethylene, also known as *ethene*, *olefiant gas*, or *heavy carbureted hydrogen*, was discovered in 1796 by four Dutch chemists, Deiman, Paets von Troostwyk, Bondt, and Lauwerenburgh.

**108. Occurrence.**—This gas is one of the most important constituents of coal gas, being formed when the coal is subjected to destructive distillation; it has been found in small quantity among the gases of coal mines.

**109. Preparation.**—Ethylene is most readily prepared by the action of sulphuric acid on alcohol, when the acid abstracts the elements of water from the alcohol:

$$\underset{\text{alcohol}}{C_2H_6O} = \underset{\text{ethylene}}{H_4C_2} + \underset{\text{water}}{H_2O}$$

This equation exhibits only the final result, the chemical change itself being evidently more complicated.

Experiment 19.—Mix in a large flask, fitted with a delivery tube, 1 part of alcohol with 5 parts of concentrated sulphuric acid, and heat very gently. Ethylene is readily evolved, and may be collected in jars over water. It will be found advantageous to mix the alcohol and acid

with dry sand to a thick paste before heating; the sand is added to prevent frothing towards the end of the evolution of the gas.

**110. Properties.**—Ethylene is a colorless, irrespirable gas, having usually an ethereal odor. It burns readily with a bright luminous flame, which evolves considerable quantities of smoke. It is soluble in about eight times its volume of water. Ethylene, on being mixed with three volumes of oxygen, explodes violently on the approach of a flame. It is decomposed by the electric spark, the carbon being deposited and twice its volume of hydrogen remaining.

Ethylene is an unsaturated substance, and unites directly with an equal volume of chlorine to an oily liquid of the composition $H_4C_2Cl_2$:

$$\underset{\text{ethylene}}{H_4C_2} + \underset{\text{chlorine}}{Cl_2} = \underset{\text{ethylene chloride}}{H_4C_2Cl_2}$$

From this property the gas received the already mentioned name of *olefiant gas*, and the liquid thus obtained has been known as the *oil of the Dutch chemists.*

EXPERIMENT 20.—To show the direct union of ethylene and chlorine, fill a glass cylinder half full of chlorine over the pneumatic trough, and then add, as quickly as possible, an equal volume of ethylene. The cylinder is then closed with a glass plate, and supported with its mouth downwards under water in a separating funnel, furnished with a glass stop-cock, as shown in Fig. 18. The volume of the mixed gases quickly begins to diminish, drops of oil being formed on the sides of the cylinder and the surface of the water. As the drops increase, they fall to the bottom of the funnel. Water must be poured into the funnel to replace that which rises into the cylinder, and when the whole of the gas mixture has disappeared, the oil may be drawn out of the funnel through the stop-cock into a test tube, in which it is shaken with a little potash to absorb any excess of chlorine that might be present. The agreeable, chloroform-like odor of the oil will then be perceived, especially on pouring it out into a shallow dish.

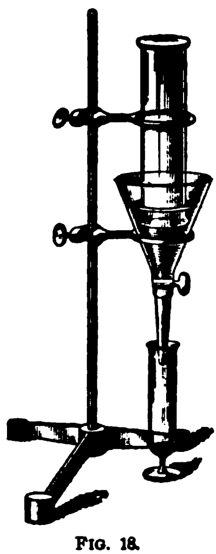

FIG. 18.

### DIHYDROGEN DICARBIDE, OR ACETYLENE.

*Formula $H_2C_2$. Density 12.97. Specific gravity .896. Molecular weight 25.94. One liter weighs 1.16 grams (12.97 criths).*

**111. History and Preparation.**—Acetylene was discovered by E. Davy in 1836, and investigated by Berthelot in 1860.

It is produced during the combustion of many hydrocarbons in a limited supply of air. Thus, when a Bunsen burner lights at the bottom of the tube, acetylene is produced in considerable quantities. It may be prepared by the direct union of carbon and hydrogen at high temperature. The most convenient method of thus preparing the gas is by passing a current of electricity, from a powerful voltaic battery, through two electrodes of carbon enclosed in a glass flask containing hydrogen.

**112. Properties.**—Acetylene is a colorless gas, with a peculiar and disagreeable odor, and is condensable to a liquid under a pressure of 68 atmospheres at 37°. It is a non-supporter of combustion, and burns with a bright, luminous, but rather smoky flame. It is quite soluble in water, and is also readily absorbed by ammoniacal cuprous chloride, forming a red precipitate of cuprous acetylide, which is explosive. This explosive body is sometimes formed in brass gas pipes by the action on them of the acetylene in coal gas, and has been the cause of fatal accidents. It unites directly with the halogens; for example, the compounds of chlorine with it are $H_2C_2Cl_2$ and $H_2C_2Cl_4$.

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### ILLUMINATING GAS.

**113. History.**—The production of a combustible gas from coal was first observed by Clayton in 1664, though it was not until 1792 that the application of this gas as a means of illumination was successfully carried out by Murdock. In

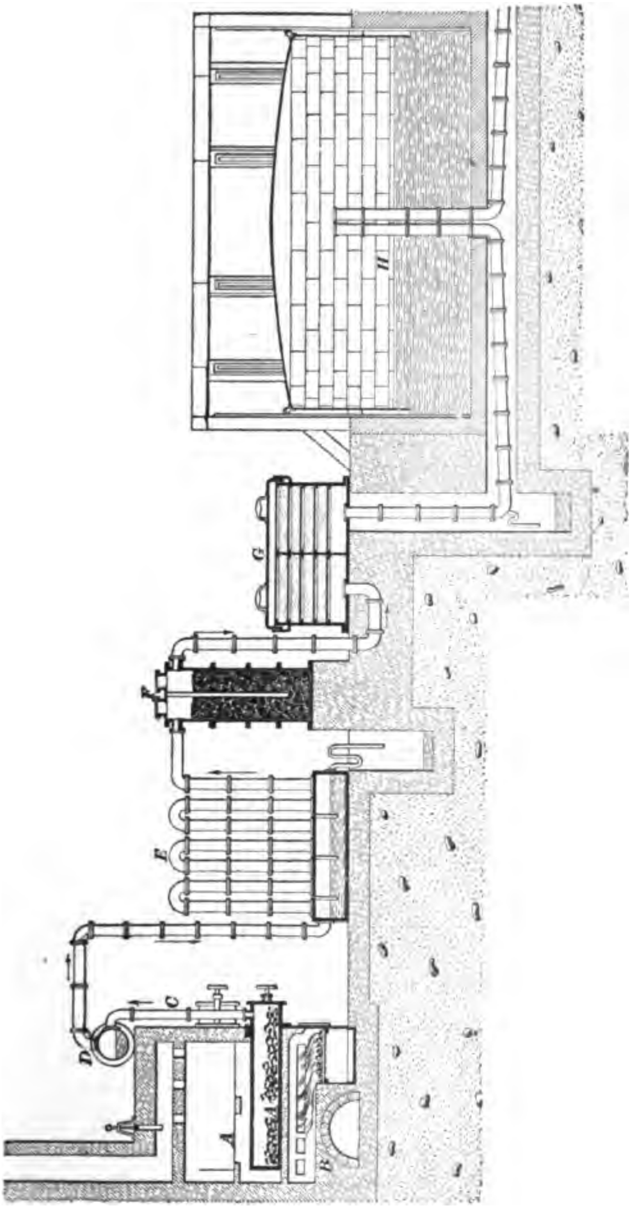


FIG. 19.

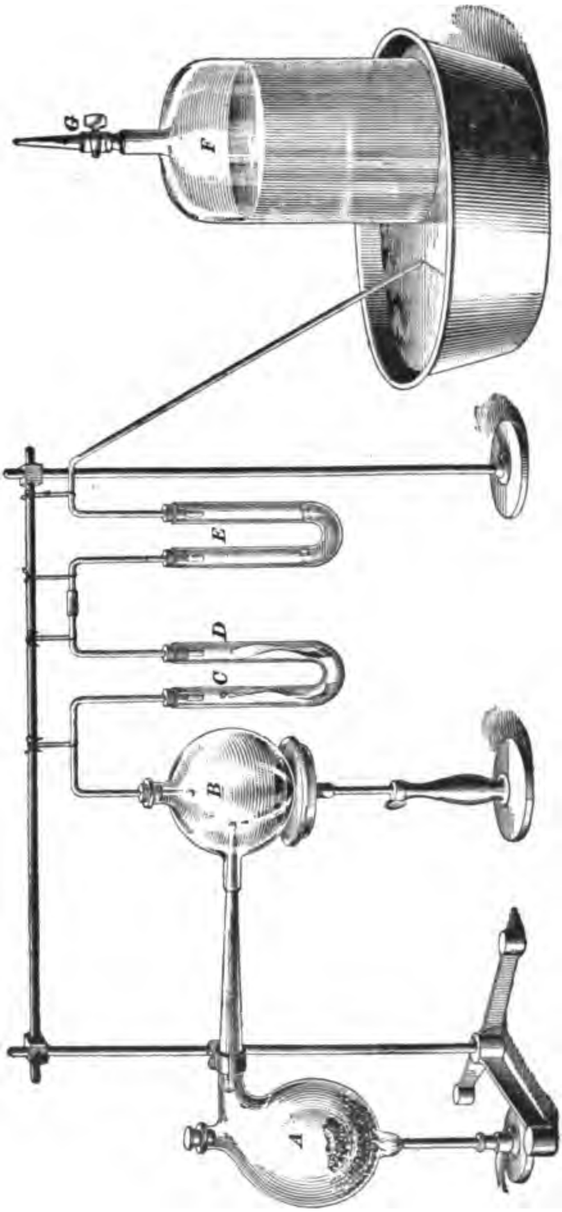


Fig. 20.

1798 he lighted in this way Boulton & Watt's works at Soho, near Birmingham, in England. The streets of London were first lighted with gas in 1812, while Paris did not adopt it until 1815.

**114. Preparation.**—Illuminating gas is manufactured by the destructive distillation of bituminous coal, though also various other products, such as petroleum, wood, resin, etc., have been employed for this purpose. The general interior arrangement of a gas works for the manufacture, purification, and collection of coal gas is shown in Fig. 19. The coal is placed in cylindrical iron retorts *A*, set in a furnace *B*. As a rule, five retorts are heated by the same fire, such a set of retorts being technically known as a *bench*. The products of the destructive distillation pass from the retort through a tube *C* up into a larger horizontal tube *D*, known as the *hydraulic main;* here the tar and a portion of the water are condensed to liquids. The gas then passes on, first through a series of vertical pipes *E*, and then through the coke box *F*—technically known as the *scrubber*—by which it is still further cooled and the condensable vapors thus separated. It finally enters the purifier *G*, which consists of a large metallic box, containing, on shelves for this purpose, either dry slaked lime, or, what is preferable, ferric hydrate mixed with lime and sawdust. From this purifier the gas issues, freed from most of its impurities, such as sulphur compounds and carbon dioxide in particular, and is collected in the adjoining *gasometer H* for distribution.

The destructive distillation of coal is frequently exhibited upon the lecturer's table with an apparatus shown in Fig. 20. The coal is placed into the retort *A*, which is strongly heated; the solid and liquid products (tar, ammoniacal liquor, etc.) distilling over are condensed in the globular receiver *B*. The gas passes on into the first **U** tube, one limb *C* of which contains some red litmus paper for the detection of ammonia, while the other limb *D* contains a piece of paper impregnated with lead acetate, to detect hydrogen sulphide, which will blacken paper thus prepared. The second **U** tube *E* contains

enough lime water to fill its bend, which indicates, by becoming milky, the presence of carbon dioxide. At last the coal gas is collected over water in the jar *F*, which is furnished with a jet *G*, from which the gas may be burned, when forced out by depressing the jar in water.

**115. Composition and Properties.**—Coal gas is a mixture of several gaseous products, which vary according to the quality of the coal employed in its manufacture, the temperature at which it is distilled, etc., but which consists essentially of hydrogen and marsh gas mixed with variable proportions of olefiant gas, acetylene, carbonous and carbonic oxides, butylene, nitrogen, oxygen, and hydrogen sulphide. Its specific gravity is about .4, and increases with the illuminating value of the gas. This illuminating value of a gas is determined by an instrument called a *photometer*, in which the amount of light given by the gas, burning from a jet at the rate of 5 cubic feet per hour, is compared with that emitted by a standard candle burning 120 grains of spermaceti in the same time. Coal gas may, under favorable circumstances, rise in its illuminating power as high as 25 to 30 candles, though the average coal gas supplied in our cities rarely amounts to more than 16 candlepower.

The constituents that contribute most largely to the illuminating value of the gas are acetylene, olefiant gas, the vapor of benzene, and similar hydrocarbons.

The most objectionable constituent is the sulphur, present as hydrogen sulphide and bisulphide of carbon; this is converted by combustion into sulphur dioxide, which seriously injures furniture, pictures, etc. The object of the manufacturer of coal gas is to remove, as far as possible, everything from it except the constituents mentioned as essential, and at the same time to obtain as large a volume of gas from a given weight of coal as is consistent with good illuminating value.

The collateral products of the coal-gas manufacture are, in general, two: the ammoniacal liquors and the gas tar. The former consists of the condensed water, holding in solution

the ammonia produced from the nitrogenous matters in the coal; the latter is a very complex substance, containing in its lighter portions certain volatile liquids, as benzene and toluene, and certain volatile alkaline bases, such as aniline and chinoline, and, in its heavier portions, certain phenols, as phenol proper (carbolic acid) and cresol; and certain hydrocarbons, as naphthalene and anthracene.

All these collateral products, as well as the destructive distillation of coal, will be more minutely treated in *Organic Chemistry.*

## CARBON AND OXYGEN.

**116.** Two oxides of carbon are known; namely, carbon monoxide $CO$ and carbon dioxide $CO_2$. The latter of these, being the most important, should be first studied.

### CARBON DIOXIDE.

*Formula $CO_2$. Density 21.945. Specific gravity 1.524. Molecular weight 43.89. One liter weighs 1.97 grams (21.945 criths).*

**117. History.**—It has been already mentioned that carbon dioxide—or *carbonic-acid gas*, as it is frequently called—is a component of the air. It was the first gas distinguished from air, being noticed as a distinct substance by Paracelsus in 1520, while soon after Van Helmont obtained it from limestone—whence he called it *chalky air*—and noticed also its production in the fermentation of sugar, and in the burning of charcoal. Black showed in 1757 that alkalies absorbed it and that its compounds effervesced with acids. Lavoisier in 1775 determined its composition synthetically by burning carbon in oxygen.

**118. Occurrence.**—Carbon dioxide is, as has been previously mentioned, a component of the air. Its proportion is greater during the night than during the day, since plants

only decompose carbon dioxide in daylight. The oleander leaf, for instance, was found to decompose, on an average, in sunlight, 1,108 cubic centimeters of $CO_2$ per square meter.

Carbon dioxide is formed chiefly by the operation of the atmospheric oxygen in supporting combustion and respiration. The substances used as fuel contain a considerable amount of carbon, which in the act of combustion combines with the atmospheric oxygen, and thus escapes into the air as carbon dioxide. In the process of respiration, the carbon dioxide is formed from the carbon contained in the blood and different portions of the animal frame to which oxygen is conveyed by the blood; the latter, in passing through the lungs, gives out, in exchange for the oxygen, a quantity of carbon dioxide produced by the union of a former supply of oxygen with the carbon of the digested food, which has passed into the blood and has not been required for the repair of wasted tissue.

The leaves of plants, under the influence of light, have the power of decomposing the carbon dioxide of the atmosphere, the carbon of which is applied to the production of vegetable compounds forming portions of the organism of the plant; and, when this dies, the carbon is restored, after a lapse of time, to the atmosphere, in the original form, i. e., carbon dioxide. If a plant is consumed as food by living beings, its carbon will eventually be converted into carbon dioxide by respiration, as has been already explained. The use of the plant as fuel, either soon after its death in the shape of wood, or after the expiration of time has converted it into coal, will naturally also consign its carbon to the air in the form of carbon dioxide. Even if the plant is left to decay, this process involves a slow conversion of its carbon into carbon dioxide by the oxygen of the air.

*Putrefaction* and *fermentation* also form very important factors in restoring to the air, in the form of carbon dioxide, the carbon contained in dead animal and vegetable matter. Although, in the minds of most people, these two processes are distinct, yet their chemical operation is certainly of the

same kind, consisting in the resolution of a complex substance into a simpler one, produced by contact with some minute living animal or plant. The discussion of the true nature of these processes would be premature at this early stage of study, and it will suffice at present to state that carbon dioxide is one of the simpler forms into which the carbon is converted by the metamorphosis that follows so quickly upon the death of animals or vegetables.

Carbon dioxide appears rather abundantly in the mineral kingdom, as it exists in vast quantities in combination with lime, in limestone, chalk, marble, etc., and also issues from the earth in some places in considerable quantities. At Nauheim, in Germany, is a spring that exhales probably 1,000,000 pounds of carbon dioxide annually. Many spring waters, as, for instance, those of Seltzer, in Germany, and many other places in this country and Europe, are very highly charged with this gas.

**119. Preparation.**—By the action of heat, limestone may be decomposed into lime and carbon dioxide, according to the following equation:

$$\underset{\substack{\text{limestone}\\\text{(calcium carbonate)}}}{CaCO_3} = \underset{\substack{\text{lime}\\\text{(calcium oxide)}}}{CaO} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2}$$

It is generally prepared by the action of an acid on some carbonate, as that of calcium or sodium.

EXPERIMENT 21.—Place some fragments of marble or limestone in the flask arranged as for the preparation of hydrogen; add a little water, and then some hydrochloric acid; collect the evolved gas over water.

The evolution of carbon dioxide by the above experiment may be expressed by the equation:

$$\underset{\substack{\text{calcium}\\\text{carbonate}}}{CaCO_3} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{2HCl} = \underset{\substack{\text{calcium}\\\text{chloride}}}{CaCl_2} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2}$$

**120. Properties.**—Carbon dioxide is a colorless gas with a slightly pungent odor and acid taste—best described

as being those of a freshly opened bottle of soda water. It is heavier than air, its specific gravity being 1.524.

At 15° and ordinary pressure, carbon dioxide is soluble in about its own volume of water; as the pressure increases—the temperature remaining constant—another volume of the gas is absorbed for each atmosphere of pressure added. As the gas, however, is condensed in the same ratio, according to Mariotte's law—*the volume of any gas is inversely and its density is directly as the pressure to which it is subjected*—it follows that the volume of the gas dissolved by water is actually the same at all pressures, while the weight is directly proportional to the pressure.

It is, as a rule, found that the greater the solubility of the gas in water, the more easily can the gas be liquefied; thus, carbon dioxide is much more easily liquefied than either hydrogen or oxygen. At about 17°, 54 atmospheres will condense carbon dioxide to a colorless, transparent liquid of specific gravity .85 (water = 1), whose boiling point is −80°. If the temperature of the gas is lowered to 0°, a pressure of 35 atmospheres will be sufficient to liquefy it.

Liquid carbon dioxide dissolves in alcohol and in ether, but not in water. When allowed to evaporate rapidly, as by pouring the liquid out in a stream from the vessel containing it, a portion of it volatilizes, and, in so doing, absorbs the heat necessary to keep the remainder in a liquid state, which, as a result, freezes. Solid carbon dioxide thus obtained is a white, snow-like mass, evaporating comparatively slowly.

EXPERIMENT 22.—A small specimen of liquid carbon dioxide is easily prepared. A strong glass tube about 12 inches long, $\frac{5}{16}$ inch in diameter in the bore, and $\frac{1}{16}$ inch thick in the walls, as shown in *A*, Fig. 21, is used. With the aid of the blowpipe flame this tube is softened and drawn off at about an inch from one of the ends, as shown in *B*, Fig. 21, which is thus closed, as represented in *C*, Fig. 21. This operation must be performed very slowly and carefully, in order to avoid the walls of the closed end becoming much thinner than the walls of the tube. When the tube has cooled, between 30 and 40 grams of finely powdered bicarbonate of ammonia are introduced into the tube and closely rammed into it by means of a glass rod. The part of the tube containing the bicarbonate is then wrapped in a few thicknesses of moist blotting paper, in order to keep it cool, and the tube is bent just beyond

the carbonate of ammonia to a somewhat obtuse angle (see *D*, Fig. 21). The tube is then softened at about an inch from the open end and drawn out to a narrow neck (*E*, Fig. 21), through which some concentrated sulphuric acid is poured down a funnel tube, so as not to soil the

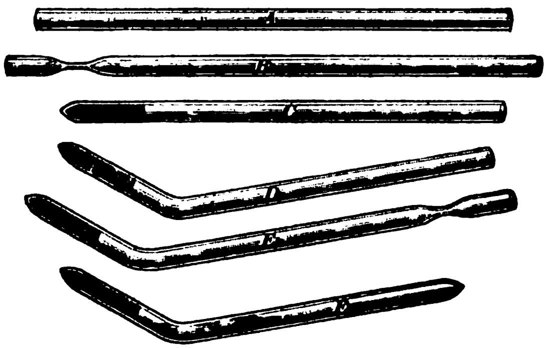

FIG. 21.

neck, which is then carefully drawn out and sealed by means of the blowpipe, as shown in *F*, Fig. 21. The empty space in the tube should *not* exceed ¼ of a cubic inch.

When the tube is thoroughly cold, it is suspended by strings in such a position that the experimenter, who, for his own safety in case of an explosion, should retire behind a screen, may reverse the tube, allowing the acid to flow into the limb containing the carbonate of ammonia.

If the tube is strong enough to resist the pressure, it will be found, after a few hours, that a layer of liquid carbon dioxide has been formed upon the surface of the solution of ammonium sulphate. By cooling the empty limb in a mixture of cracked ice and salt, the liquid carbon dioxide can be made to distil itself over into this limb, leaving the ammonium sulphate behind in the other.

Liquid carbon dioxide may be obtained on a larger scale by using the apparatus invented by Thilorier, in which the gas is liquefied by its own pressure, or that of Natterer, in which the pressure is produced mechanically.

Fig. 22 represents Bianchi's modification of Natterer's condensing pump. The piston is solid, and is worked by a crank and flywheel, as represented in the figure. The receiver at the top of the pump barrel is made of heavy bronze, and has a tight valve below, and a screw plug above, by which the liquefied carbon dioxide may be drawn off.

The tube leading to the pump serves to convey the carbon dioxide. As the pump is worked, the pressure in the receiver increases until it reaches about 38.5 atmospheres—the receiver being packed in ice—when each additional stroke of the pump liquefies the gas forced into it. In this way, half a kilogram of liquid carbon dioxide may be obtained in a very short time. The receiver is then removed from the pump and inverted, and the gas allowed to escape into a peculiarly constructed cylindrical box of metal, which, in the course of a few seconds, is filled with the carbon dioxide snow.


FIG. 22.

Although carbon dioxide is not poisonous when taken into the stomach, it is fatal to animal life when inhaled; even largely diluted with air, it exerts a narcotic action on the system, and has been proposed, owing to this property, as an anesthetic.

The poisonous effects of this gas, when inhaled, may be traced back to the fact that the inhaled gas offers an obstacle to the escape of the carbon dioxide, by diffusion, from the blood of the venous circulation in the lungs and its consequent replacement by the oxygen necessary to arterial blood. Any hindrance to this interchange must impede respiration, and such hindrance would, of course, be afforded by carbon dioxide present in the air inhaled, in proportion to its quantity.

Owing to the difference in temperament and constitution of individuals, it is impossible to establish an exact general rule as to the precise quantity of carbon dioxide that may be present in the air without injury to respiration; but it may be safely said that it is not advisable to breathe for any

length of time in air containing more than $\frac{1}{1000}$ (.1 per cent.) of its volume of carbon dioxide. As carbon dioxide is the only gas that renders clear lime water *milky*, the fact whether the air of a room contains too much of this gas may be easily ascertained by shaking half a measured ounce of lime water in a half-pint bottle of air; if the lime water becomes turbid, the air is not wholesome to breathe and should be ventilated in some way.

There appears to be no immediate danger, however, until the carbon dioxide amounts to $\frac{1}{200}$ (.5 per cent.), when most persons are attacked by the languor and headache attending the action of this gas. A larger proportion causes insensibility, and air containing $\frac{1}{12}$ of its volume causes suffocation.

The danger in entering old wells, cellars, and other confined places, is due to the accumulation of carbon dioxide, either exhaled from the earth or produced by decay of organic matter; the gas is also freely generated in brewing and other similar processes of fermentation, and many deaths have occurred through men incautiously descending into the vats used in breweries, etc., after the liquor had been drawn off, forgetting that the carbon dioxide, being heavier than air, still hovers in the vat. Carbon dioxide also constitutes the so called *choke damp*, or *after damp*, frequently encountered in collieries.

Carbon dioxide possesses the property of extinguishing combustion. A lighted taper plunged into it has its flame extinguished at once.

It will be remembered by the student that pure nitrogen is also capable of extinguishing the flame of a taper, but a large proportion of this gas may be present in air without affecting the flame, whereas a taper is extinguished in air containing one-eighth of its volume of carbon dioxide, and is sensibly diminished in brilliancy by a much smaller proportion of the gas.

**121. Determination of Carbon Dioxide.**—The ready liberation of carbon dioxide from carbonates by the action of acids as shown in Experiment 21, affords a ready and

comparatively simple means of determining by direct weighing the amount of that gas in a carbonate. A number of forms of apparatus have been devised for that purpose, but one of the most simple and convenient is that known as *Schrötter's carbon-dioxide apparatus.* The apparatus, the illustration of which is shown in Fig. 23, consists of a very light flask $A$, fitted with a stopper $B$ in the side. To the right, on the top, is shown a small reservoir $D$, provided with a stopper and stop-cock $C$, from which latter a bent tube $E$ leads to the bottom of the flask. To the left is an exit tube $F$, enclosed within another tube $G$, which in its turn is contained within the tube $H$. This latter is provided with a stopper $I$ pierced with a small hole. The arrangement of the tubes $F$, $G$, and $H$ is provided for the purpose of drying the escaping gas, which finds its way up through $F$ and $G$, then through some holes at the bottom of $G$ leading into the outer space, and then up between $G$ and $H$, and out through the stopper $I$.

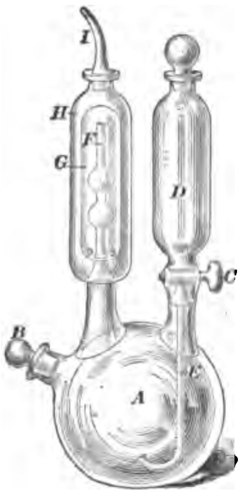

FIG. 23.

EXPERIMENT 23.—To make the determination of carbon dioxide, thoroughly clean the apparatus shown in Fig. 23 and previously described; close the stop-cock $C$, and fill the reservoir $D$, by means of a pipette or small funnel, with dilute sulphuric acid—1 part of acid to 2 parts of water; then take out the stopper $I$, and with the aid of a small funnel carefully fill $H$ to about two-fifths of its height with concentrated sulphuric acid. No acid must be spilled on the outside of the apparatus during either of these operations, and, if possible, the inside of the necks of the two reservoirs must not be wetted. Next introduce 10 cubic centimeters of water in the flask, part $A$, through the opening $B$. The apparatus being now ready for the determination, as a final precaution take out the stoppers $B$, $C$, $I$, and see that they are perfectly dry and clean; if not, wipe each on a piece of old cloth, and with the same wipe also the inside of the necks of the various openings. Handle the apparatus as little as possible with the warm hand, and during these last cleanings remove the stopper at $B$. Meantime, take some pure anhydrous sodium carbonate, and heat a quantity of about 5 grams

in a crucible over the flame of a Bunsen burner, so as to drive off all traces of moisture. Place a watch glass on the pan of the balance, and weigh it carefully; then add to the weights 1.06 grams, and weigh off that quantity of the sodium carbonate. At the end, you will find it the most convenient way to take a little off or add a little with the point of the blade of a fine, perfectly dry and clean penknife, until the exact weight is obtained. Then introduce a *dry*, wide-stemmed funnel in *B* of the apparatus, and pour in the 1.06 grams of the carbonate, taking great care that none whatever is lost. To do this, it is a good plan to fit the apparatus obliquely in a stand fitted with a clamp, so that the tubulure *B* is upright. Brush carefully the whole of the carbonate out of the watch glass, on which it was weighed, with a dry, clean camel's-hair brush, and finally brush out the funnel also into the apparatus. Replace the stopper, and weigh the whole apparatus accurately.

Run in the acid slowly and carefully, by removing the stopper of *D* and slightly turning the stop-cock *C*, so as to maintain a steady current of evolved carbon dioxide. As carbon dioxide, however, is soluble, to a certain extent, in water, it is necessary at the close to heat the apparatus gently, in order to drive off the gas dissolved in the water in *A*. For this purpose, place a clean iron plate on a tripod stand and heat it with the Bunsen burner. Stand the apparatus on top of the hot plate. Watch the liquid; you will notice that, as it grows hot, fine bubbles of gas escape. Continue a gentle heating until the evolution of the gas ceases. The apparatus may be allowed to get so hot as just not to be borne by the hand, but the liquid it contains must, on no account, be permitted to boil. Nothing can now have escaped from the apparatus but air and carbon dioxide, as any water vapor that might accidentally be evolved will have been arrested and absorbed by the concentrated acid in *F*, *G*, and *H*. While still hot, air should be drawn through the apparatus, in order to remove all the carbon dioxide evolved; but, as the air is usually moist, it is evident that thus drawing moist air into *A*, and drying the same as it makes its exit through *F*, *G*, *H*, will tend to increase the weight of the whole apparatus by absorption of water vapor from this air. To obviate this, remove the stopper *C*, and introduce in its place a cork and leading tube, which latter is connected to the exit tube of a small wash bottle containing concentrated sulphuric acid. Slip a piece of rubber tubing over the perforated stopper *I*, and gently suck a current of air through the apparatus until the carbon dioxide is removed. As carbon dioxide has a distinct taste, as has been previously mentioned, this affords considerable guidance in determining when the whole gas is removed. Next allow the apparatus to become perfectly cold, remove the cork from *C* and the rubber tube from *I*, replace the stopper *C*, and weigh. Again draw air through in the same way, and weigh again; continue this as long as there is any loss of weight. Take the lowest weight as the most correct.

Proceed, in the next place, to make a similar determination on pure calcium carbonate, for which purpose take some fragments of crystallized calcite (Iceland spar); dry them in an oven and weigh off exactly 1 gram. In charging the Schrötter apparatus, employ dilute nitric acid, 1 part of acid to 1 part of water, instead of sulphuric acid, for filling *D*, the reason being that calcium sulphate is only very slightly soluble in water. In other respects, proceed with the determination precisely as before. It is not necessary to reduce the calcite to a powder, as small fragments lend themselves better to a steady and a manageable current of gas.

**122.** The method of procedure is illustrated by the record of an experiment, performed by the instructor for this purpose:

| | |
|---|---|
| Weight of watch glass ................ | 4.83 grams |
| Weight of sodium carbonate.......... | 1.06 " |
| | 5.89 grams |
| Weight of Schrötter apparatus before.. | 59.72 grams |
| Weight of Schrötter apparatus after... | 59.27 " |
| Weight of evolved carbon dioxide..... | .45 gram |

On calculating the molecular weight of sodium carbonate from its formula, $Na_2CO_3$, it will be found to be 106, and in the experiment we have taken 106 centigrams (1.06 grams) and have 45 centigrams (.45 gram) of carbon dioxide evolved. This determination affords practical proof of the fact that the action of sulphuric acid in sodium carbonate is represented by the following equation:

$$\underbrace{Na_2CO_3}_{\substack{106 \\ 106}} + H_2SO_4 = \underbrace{CO_2}_{\substack{44 \\ 45}} + H_2O + Na_2SO_4$$

| | | | |
|---|---|---|---|
| *Molecular weight* | 106 | | 44 |
| *Taken* | 106 | *Found* | 45 |

Similarly, in the case of calcium carbonate, the molecular weight, 100, has been taken, and the evolved gas should also weigh, as nearly as possible, 44 centigrams.

**123.** Carbon dioxide may be separated from most other gases by the action of potash, which readily absorbs it and combines with it to form potassium carbonate, according to the equation:

$$\underset{\substack{\text{potash} \\ \text{(potassium hydroxide)}}}{2KHO} + CO_2 = K_2CO_3 + H_2O$$

The proportion of carbonic-acid gas is inferred, either from the diminution in volume suffered by the gas when treated with potash, or from the increase of weight of the latter.

In the case of the former, the gas is carefully measured over mercury, Fig. 24, with due attention to temperature and atmospheric pressure, and a little concentrated solution of potash is thrown up through a curved pipette or syringe, introduced into the opening of the measuring tube beneath the surface of the mercury. The tube is gently shaken for a few seconds, to promote the absorption of the gas, and, after a few minutes' rest, the diminution of volume is read off. Instead of solution of potash, moist potash in the solid state is sometimes introduced in the form of small sticks or balls, which are attached to a bent wire.

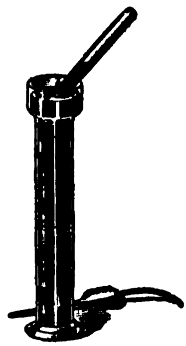

FIG. 24.

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### CARBONIC ACID.

*Formula* $H_2CO_3$. *Molecular weight 61.85.*

**124.** Carbonic acid is produced by the solution of carbon dioxide in water, according to the equation:

$$CO_2 + H_2O = H_2CO_3$$

It is, however, unstable, and has not been obtained free from water, decomposing too readily into water and carbon dioxide on slightly raising the temperature or by freezing it.

The solution in water is distinctly, though feebly, acid. It possesses the pungent odor and agreeable acid taste so well known in so called soda water, which, in fact, is simply made by dissolving carbon dioxide in water under a certain amount of pressure.

**125. Salts Formed by Carbonic Acid.**—Although so ready to combine with the alkalies and alkaline earths, as

shown in its absorption by potash and by lime water, carbonic acid must be classed among the weaker acids. It does not neutralize the alkalies completely, and it may be displaced from its salt by most other acids. Its action on the coloring matter of litmus is feeble and transient.

EXPERIMENT 24.—Pour a little blue litmus solution into a jar of the acid; a wine-red liquid is produced, which becomes blue again when boiled, losing its carbon dioxide.

If you compare the red color of litmus solution obtained by sulphuric, nitric, or hydrochloric acid, you will find that the red color produced by these acids is not only much brighter, but also does not disappear on boiling.

With each of the alkalies, carbonic acid forms two well defined salts, the *carbonate* and the *bicarbonate*. Thus, the carbonates of potassium and sodium are represented by the formulas $K_2CO_3$ and $Na_2CO_3$, respectively; while the bicarbonates are represented by the formulas $KHCO_3$ and $NaHCO_3$. The existence of the latter compounds is a proof of the existence of $H_2CO_3$, although this compound, as previously mentioned, has not been obtained in the separate state.

The formula $H_2CO_3$ represents carbonic acid as dibasic, that is, an acid containing 2 atoms of $H$ which may be replaced by metals (see Art. **59**, *Theoretical Chemistry*).

Carbonates may be *normal*, *acid*, or *basic*. A normal carbonate is one in which all the hydrogen in $H_2CO_3$ is replaced by a metal or group of metals, as in sodium carbonate $Na_2CO_3$, and calcium carbonate $CaCO_3$.

An acid carbonate is one in which only half of the hydrogen is replaced by a metal, as in hydrosodium carbonate $NaHCO_3$.

A basic carbonate is a normal carbonate in combination with a hydrate of the metal, as in white lead, basic lead carbonate $2PbCO_3Pb(OH)_2$.

**126. Solubility of Bicarbonates.**—Several of the bicarbonates are soluble in water, while the corresponding carbonates are insoluble. That of calcium is an interesting and important example.

EXPERIMENT 25.—Boil some hard water, taken from springs found in chalk or limestone formations (if obtainable), in a beaker or small flask for about 15 minutes; at the expiration of that time, note that the water has become slightly turbid by the separation of calcium carbonate.

The bicarbonate has been decomposed by heat, the carbon dioxide evolved, and the insoluble carbonate precipitated:

$$\underset{\text{calcium bicarbonate}}{CaH_2(CO_3)_2} = \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2}$$

**127. Hard and Soft Waters.**—In Experiment 25, reference has been made to *hard water;* the inference may be drawn that hardness is in some way connected with the presence of calcium salts in solution. It may be well to explain here what is understood by the terms *hard* and *soft* when applied to water, and to what these properties are due.

The student will have noticed, from daily experience, that certain kinds of water, when mixed with a very small quantity of soap, immediately produce a lather, and that the water acquires that peculiar feel to the hands, which is generally known as *soapiness.* Such water is termed *soft water.* Other waters, when used with soap for washing purposes, do not lather at all readily, and do not cause soapiness until a considerable quantity of soap has been consumed. When lather is actually formed, there will be found, on examination, a layer of scum on the surface of the water. Such water is termed *hard water.*

Without going into the details of the composition of soap and its reaction with water when used for washing, it may be explained that soluble salts of calcium and magnesium decompose soap, forming a precipitate which constitutes the previously mentioned scum found when washing with hard water. Consequently, if water containing calcium salts in solution is employed for washing purposes, sufficient soap must first be added to precipitate these salts before any is available for cleansing; hence, hard waters are neither so agreeable nor so economical for washing purposes.

The principal calcium and magnesium salts found in water are the carbonate and the sulphate. As seen from

Experiment 25, the carbonates may be precipitated by the act of boiling, and any hardness due to their presence may be thus remedied. Consequently, any hardness produced by carbonates of calcium or magnesium is termed *temporary hardness*, because such hardness may be removed by boiling.

The sulphates and chlorides of calcium and magnesium are not precipitated by boiling, as their solution is caused by the water itself, and not by water plus carbon-dioxide gas. Therefore, hardness due to the presence of sulphates (or chlorides) of calcium or magnesium is called *permanent hardness*.

The hardness of most waters is partly temporary and partly permanent, the two together constituting what is known as the *total hardness* of the water.

**128.** The hardness of the water is usually tested by taking a measured quantity of the water and adding thereto in a stoppered bottle a solution in alcohol of soap of a known strength. This is introduced in small quantities at a time from a measuring instrument, such as a burette, the water being well shaken after each addition. When the lather thus produced stands unbroken for about five minutes, the quantity of soap solution used is read off, and from this the total hardness is determined. A sample of the water is next boiled until the carbonates are precipitated; then after certain precautions the hardness is again determined with the soap solution. This gives the permanent hardness, which is the difference between the total and the temporary hardness.

**129. Processes of Softening Water.**—Water may be softened, to the extent of the removal of the temporary hardness, by the act of boiling for some minutes. Potassium and sodium carbonates precipitate calcium and magnesium salts, and themselves possess *detergent*, or washing, properties; therefore, these salts will remove all hardness, whether temporary or permanent. One of the characteristics of potassium and sodium carbonates is the power they possess of imparting a soapy feeling to pure water. Ordinary washing soda, or soda crystal, is commercial sodium carbonate.

**130. Clark's Water-Softening Process.**—A most interesting method for the softening of water is the one named *Clark's process.* This process depends on two chemical reactions with which the student is already familiar: *first*, that calcium carbonate is no longer soluble in water from which the carbon dioxide has been removed; *second*, that lime forms an insoluble compound with carbon dioxide. To soften water by Clark's process, lime water is added in sufficient quantity to exactly combine with the dissolved carbon-dioxide gas. The whole of the calcium, both that originally present in the water as bicarbonate and that added as hydrate, is precipitated, and the temporary hardness is thus removed. The chemical reaction is represented in the following equations:

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$

| $CaH_2(CO_3)_2$ | $Ca(OH)_2$ | $2CaCO_3$ | $2H_2O$ |
|---|---|---|---|
| soluble calcium bicarbonate | lime water (calcium hydrate) | insoluble calcium carbonate formed from the bicarbonate and hydrate | water |

The precipitated calcium carbonate is removed either by allowing it to subside or by filtration.

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### CARBON MONOXIDE, OR CARBONYL.

*Formula CO. Density 13.965. Specific gravity .967. Molecular weight 27.93. One liter of the gas weighs 1.25 grams (13.965 criths).*

**131. History.**—Carbon monoxide was discovered by Lassone in 1776, and independently by Priestley in 1783; its true nature and exact composition were determined by Woodhouse in 1800.

**132. Occurrence.**—Every one is familiar with the appearance of a coke or charcoal fire, or of a coal fire that has burned perfectly clear and smokeless—the whole mass glows with a bright red heat, and hovering over the top are

lambent blue flames. The origin of these may be traced in this way: In the lower parts of the grate, where air enters the fire, carbon dioxide is formed according to the following equation:

$$C + O_2 = CO_2$$

This carbon dioxide makes its way upwards through the red-hot carbon, and becomes changed by reduction to carbon monoxide, and thus an inflammable gas is produced. The same effect is produced in the following manner:

EXPERIMENT 26.—Loosely fill an iron tube with fragments of charcoal; fit to each end corks with pieces of quill tube passed through; place it in a furnace and raise to a red heat. Then pass a slow current of carbon dioxide through the tube and light the gas as it emerges; it burns with the same blue flame as is seen playing over a coke or charcoal fire.

Evidently, then, the gas is changed; for carbon dioxide is non-inflammable. The change is thus represented:

$$CO_2 + C = 2CO$$

When carbon is burned without a sufficient supply of air, carbon monoxide is formed as one of the products of combustion.

**133. Preparation.**—Additional to the reaction described in Experiment 25, carbon monoxide may be prepared by heating within an iron cylinder a mixture of calcium carbonate (chalk) and charcoal. The calcium carbonate is decomposed into calcium oxide and carbon dioxide, which latter is converted by the charcoal into the monoxide.

A mixture of carbon monoxide and free hydrogen is produced in abundance by passing steam over or through charcoal heated to bright redness; the reaction occurring may be expressed by the following equation:

$$C + H_2O = CO + H_2$$

It may further be prepared by the incomplete combustion of carbon, as when charcoal and blacksmith's scales (ferrosoferric oxide) are heated together, according to the equation:

$$Fe_3O_4 + 4C = Fe_3 + 4CO$$

For laboratory purposes the gas is most conveniently prepared by heating certain organic compounds with concentrated sulphuric acid. This body has, as we have already frequently seen, a very great attraction for water, in virtue of which it decomposes many substances containing hydrogen and oxygen, and assimilates the water, the remaining atoms rearranging themselves into whatever other compounds are possible.

Oxalic acid, when treated in this manner, is split up into water, carbon dioxide, and carbon monoxide, thus:

$$\underset{\text{oxalic acid}}{H_2C_2O_4} = \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{carbon monoxide}}{CO}$$

**Experiment 27.—For the preparation of carbon monoxide from oxalic acid, such an apparatus as is shown in Fig. 25 is needed. The oxalic**

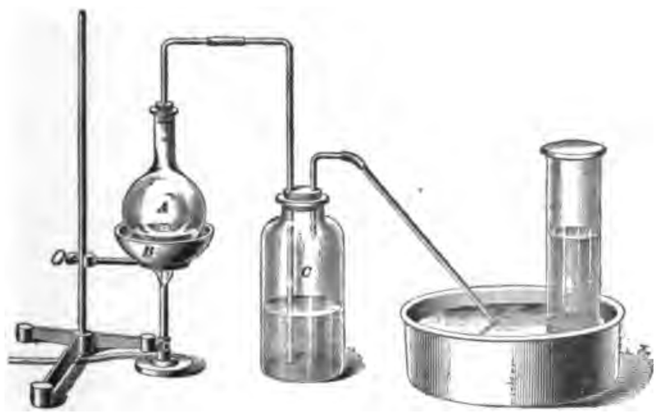

Fig. 25.

**acid (crystallized) is placed in the flask *A* and enough sulphuric acid is added to just cover it. The whole is heated in an iron cup filled with sand (sand bath) *B*. The gases as evolved pass into a washing bottle *C*, which is about half filled with a concentrated solution of potassium hydroxide (caustic potash); in bubbling through this solution the carbon dioxide is absorbed, and the carbon monoxide, thus purified, may be collected over water in the pneumatic trough. As this gas is very poisonous, great care should be taken in its preparation.**

Formic acid $HCHO_2$ on being similarly heated with

concentrated sulphuric acid, yields pure carbon monoxide, according to the following equation:

$$HCHO_2 = H_2O + CO$$

Another method is to heat potassium ferrocyanide (yellow prussiate of potash $K_4FeC_6N_6$) with sulphuric acid; the change occurring is rather complicated, but may be expressed by the equation:

$$\underset{\text{potassium ferrocyanide}}{K_4FeC_6N_6} + \underset{\text{sulphuric acid}}{6H_2SO_4} + \underset{\text{water}}{6H_2O}$$

$$= \underset{\text{potassium sulphate}}{2K_2SO_4} + \underset{\text{ferrous sulphate}}{FeSO_4} + \underset{\text{ammonium sulphate}}{3(NH_4)_2SO_4} + \underset{\text{carbon monoxide}}{6CO}$$

When carbon monoxide is required in a state of absolute purity, the former of these last two methods is preferable. The latter, though yielding this gas in larger quantities, is, as a rule, accompanied by traces of carbon dioxide as a contamination.

Experiment 28.—Take a 32-ounce flask and fit it up with a thistle funnel and leading tube, as shown in Fig. 26. The end of this thistle funnel must be pushed down as far as possible without touching the bottom of the flask. Insert, in lumps, a quarter of an ounce (7.09 grams) of commercial ferrocyanide (the quantity in cubic centimeters can in this case not very well be given, owing to the irregular size of these lumps, so, in order to be as accurate as possible, the weights are only mentioned) and about 2 ounces (56.7 grams) of sulphuric acid. Fix the flask in the retort stand with the end of the leading tube in the pneumatic trough; apply heat carefully. As soon as the gas begins to be evolved, remove the flame, as the action continues with extreme rapidity. When the air is entirely expelled, the given quantities being sufficient to fill three pint jars, collect the gas over water. Sometimes, through lack of sufficient precautions, the gas is produced so violently that the pressure forces the boiling acid up through the funnel. Should this occur, remove the burner at once, take the delivery tube out of the water, and keep well out of the reach of the splashes of falling acid.

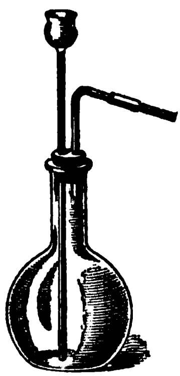

Fig. 26.

EXPERIMENT 29.—Place a light to one jar filled with the gas; notice that the gas burns with a blue flame.

**134. Properties.**—Carbon monoxide is a colorless gas; it possesses a peculiar oppressive odor and is extremely poisonous, producing a painful headache even when present in small quantities in the air. It liquefies only under very great cold and pressure (—139.5° and 35.5 atmospheres). It is only slightly soluble in water, 100 volumes of which dissolve 2.434 volumes of the gas at 15°. It is readily combustible, burning in the air (as seen by Experiment 28) or in oxygen with the characteristic lambent blue flame mentioned in Art. **132.** Though inflammable, it is not a supporter of combustion. When burned, its own volume of carbon dioxide is produced, half of its own volume of oxygen being required:

$$2CO + O_2 = 2CO_2$$

It is totally irrespirable, being an active narcotic poison, one per cent. of it in the air proving fatal.

Carbon monoxide is devoid of acid properties, and, consequently, is without action on lime water.

EXPERIMENT 30.—Add some lime water to a jar of the gas and shake up; no turbidity is produced. Inflame the gas, replace the glass plate and then shake again; the lime water becomes milky through the presence of carbon dioxide produced by combustion.

Carbon monoxide acts as a powerful reducing agent, and is frequently used in metallurgical operations for the production of metals from their oxides.

EXPERIMENT 31.—Arrange a piece of combustion tubing, about 18 inches in length, in the combustion furnace, and connect—by means of a cork, a piece of quill tubing, and a rubber tube—with an apparatus evolving carbon monoxide. (The most convenient method of obtaining the gas for this purpose is from oxalic acid and sulphuric acid. The gas may be passed through a wash bottle containing a concentrated solution of caustic potash, but the carbon dioxide takes no part in the reaction.) Partly fill the combustion tube with granulated copper oxide, expel the air by passing through it a slow current of carbon monoxide, and then light the furnace. On the tube becoming red hot, notice that the oxide of copper is reduced to the metallic state.

If wished, carbon monoxide free from the dioxide may be prepared and used for this experiment; and the gas, after its passage through the red-hot copper oxide, may be passed into lime water. The precipitate of calcium carbonate shows the production of carbon dioxide from the reaction of the monoxide and copper oxide on each other.

The following equation shows the chemical change that occurs during this experiment:

$$CuO + CO = Cu + CO_2$$

This experiment is one that the student cannot perform by himself; but, being a typical experiment performed upon the lecturer's table, and one so clearly showing the reducing power of carbon monoxide, it appears highly desirable that the student should become acquainted with it.

**135.** The poisonous character of carbon monoxide is raised as a serious objection to the use of this gas for illuminating purposes, and it has been the occasion of legislative interference—the amount of carbon monoxide permissible in a gas for illuminating being now fixed by law in most states.

The character of the flame of carbon monoxide by itself appears to afford little promise of its utility as an illuminating agent, but that it can be advantageously employed as such is easily demonstrated by kindling a jet of the gas which has been passed through a wide tube containing a little cotton moistened with rectified coal naptha (benzine), when the carbon monoxide will be found to burn with a very luminous flame.

The carbon monoxide destined to be employed for illuminating purposes is prepared by passing steam over white-hot coke, a mixture of carbon monoxide and hydrogen being thus produced:

$$C + H_2O = CO + H_2$$

This so called *water gas* contains some carbon dioxide, the quantity being greater, the lower the temperature of the coke, owing to the fact that at lower temperatures the coke burns in steam to carbon dioxide, and not to carbon monoxide:

$$C + 2H_2O = CO_2 + 2H_2$$

The average composition of water gas is generally given as follows:

| | |
|---|---|
| Hydrogen.......................... | 50% |
| Carbon monoxide................... | 40% |
| Carbon dioxide.................... | 5% |
| Nitrogen (from the air and coke)... | 5% |
| | 100% |

Since neither hydrogen nor carbon monoxide possess any sensible odor, this mixture would not be detected in the atmosphere of a room where there was a leaking gas pipe, and the presence of the poisonous carbon monoxide would remain unsuspected. Thus, it becomes incumbent on those supplying this gas to dwelling houses, etc., to render it, by mixing some gas or vapor with it, at least as odorous as is ordinary coal gas, the escape of which is so easily detected by its smell.

The application of water gas as an illuminating agent is mostly limited to its admixture with coal gas, whereby it is rendered luminous by hydrocarbons obtained from the destructive distillation of coal or petroleum.

The ready passage of carbon monoxide through heated cast iron, and its consequent presence in rooms heated by stoves of this metal, has been assumed as the cause of serious disease in many instances. With sufficient ventilation, however, no danger from this cause need be feared.

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### SUMMARY.

**136.** There exist two oxides of carbon—carbon monoxide and carbon dioxide.

Carbon dioxide occurs in the atmosphere and in combination with lime in limestone; it is most conveniently prepared by the action of an acid, as of hydrochloric upon limestone. It is a colorless gas, with a very faint odor and taste; it may be condensed by pressure; it is soluble in water, is half as heavy again as air, and remains through its weight for a long

time in the bottom of brewer's vats, old wells, etc.; it is non-inflammable and a non-supporter of combustion of most substances, but allows certain metals, as potassium and magnesium, to burn in it. The solution of the gas is slightly acid to litmus; it forms a series of important salts.

Carbon monoxide is formed in the burning of coke by the deoxidation of carbon dioxide; the same change occurs if carbon dioxide is passed over red-hot charcoal in an iron tube. The gas is more generally prepared by the action of sulphuric acid on some organic bodies, as oxalic or formic acid, or potassium ferrocyanide.

Carbon monoxide is a colorless gas, with a faint, oppressive odor; it is very poisonous; it is slightly soluble in water. It is inflammable and is a non-supporter of combustion; it is devoid of acid properties. It is a powerful reducing agent.

**137. Combustion of Marsh Gas, Acetylene, and Ethylene.**—The combustion of these three bodies affords some very interesting and instructive examples of the laws of combination by volume. Subjoined are the molecular equations representing the reactions that occur, together with those of some other examples of combustion already familiar to the student:

$$\underset{\text{1 volume}}{CH_4} + \underset{\text{2 volumes}}{2O_2} = \underset{\text{1 volume}}{CO_2} + \underset{\text{2 volumes}}{2H_2O}$$

$$\underset{\text{2 volumes}}{2C_2H_2} + \underset{\text{5 volumes}}{5O_2} = \underset{\text{4 volumes}}{4CO_2} + \underset{\text{2 volumes}}{2H_2O}$$

$$\underset{\text{1 volume}}{C_2H_4} + \underset{\text{3 volumes}}{3O_2} = \underset{\text{2 volumes}}{2CO_2} + \underset{\text{2 volumes}}{2H_2O}$$

$$C + \underset{\text{1 volume}}{O_2} = \underset{\text{1 volume}}{CO_2}$$

$$\underset{\text{2 volumes}}{2CO} + \underset{\text{1 volume}}{O_2} = \underset{\text{2 volumes}}{2CO_2}$$

$$\underset{\text{2 volumes}}{2H_2} + \underset{\text{1 volume}}{O_2} = \underset{\text{2 volumes}}{2H_2O}$$

$$\underset{\text{1 volume}}{H_2} + \underset{\text{1 volume}}{Cl_2} = \underset{\text{2 volumes}}{2HCl}$$

These equations show to a nicety the relation existing between the volumes of gases and the respective volumes of oxygen required for their combustion. They afford additional illustrations of the method of deducing these quantities from the molecular equations.

*As gaseous molecules are assumed* (at the same temperature and pressure) *to occupy the same space* (see Art. **24**, *Theoretical Chemistry*), *it follows that the number of molecules of any gas participating in a chemical change represents the number of volumes of the gas concerned.*

**138. Combustibles.**—It has been stated in Art. **104**, *Theoretical Chemistry*, that combustion is an act of burning, or, to be more explicit, a chemical combination that is so intense as to raise the products to a temperature at which they emit light. It is commonly restricted, however, to the direct union of a substance with oxygen.

It is evident that at least two substances must be concerned in every combustion: the *combustible*, i. e., the body that burns; and the *supporter of combustion*, i. e., the gas in which the combustion takes place.

Those substances that serve as combustibles are naturally very numerous. Illuminating gases—coal and water gas—have been already mentioned. Of liquids, the vegetable oils known as rape, olive, and turpentine, the animal oils called sperm and lard, and the mineral oils derived from petroleum may be here quoted. Of solids from the vegetable kingdom, wood and bayberry wax; from the animal, tallow and its product, stearin; and from the mineral, paraffin and the various sorts of coal, are examples.

All these substances, though so different in character and origin, agree in the fact that they contain carbon and hydrogen. Some contain oxygen in addition.

**139. Heat of Combustion.**—Not only do substances in burning give out heat, but *the amount of heat evolved by the combustion (or combination with oxygen) of a given weight of any substance is always the same.* Thus, whether the substance be burned slowly or rapidly, provided it is burned to

the same products of combustion, the total amount of heat generated never varies. Table 2 gives the number of heat units evolved by the combustion in oxygen and chlorine, respectively, of 1 gram of each substance.

The student is reminded that a heat unit is the quantity of heat necessary to raise 1 gram of water from 0° to 1°.

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TABLE 2.

HEAT DEVELOPED DURING COMBUSTION.

| Substance. | In Oxygen. Heat Units. | In Chlorine. Heat Units. |
|---|---|---|
| Hydrogen | 34,462 | 24,087 |
| Carbon | 8,080 | |
| Sulphur | 2,220 | |
| Phosphorus | 5,747 | 3,422 |
| Carbon monoxide | 2,634 | |
| Marsh gas | 13,063 | |
| Olefiant gas | 11,942 | |
| Alcohol | 6,909 | |

Of the elements, hydrogen develops by far the greatest amount of heat on combustion, the next place being taken by carbon. Of the various compounds of carbon, the student will observe that carbon monoxide, during its further combustion to carbon dioxide, evolves also a considerable quantity of heat.

It will be of interest to compare the amount of heat evolved in the two stages of oxidation of carbon. As carbon monoxide contains, according to its formula, $\frac{12}{28}$ of its weight of carbon, it is evident that 1 gram of carbon would yield $\frac{28}{12}$ grams of carbon monoxide, and, consequently, that 1 gram of carbon as monoxide would, in its further oxidation to carbon dioxide, evolve

$$\frac{2,634 \times 28}{12} = 6,146 \text{ heat units}$$

But the total number of heat units evolved by the complete combustion of carbon is 8,080. Therefore, 1 gram ot carbon evolves in oxidation to the monoxide

$$8{,}080 - 6{,}146 = 1{,}934 \text{ heat units,}$$

and during further oxidation to the dioxide, 6,146 heat units. The student knows that when the carbon dioxide formed in a fire of carbon passes upwards through red-hot carbon, it is reduced to the monoxide, which in its turn burns on the upper surface of the fire, where there is free access to air. Whenever carbon is burned with a limited supply of oxygen, as where a draft of air is drawn through a furnace containing large quantities of coke or other forms of carbon, the monoxide is the chief product of combustion. This cannot burn until it reaches the air; and accordingly, in the older forms of furnaces used in metallurgical operations, particularly the blast furnace used for the smelting of iron ores, enormous quantities of carbon monoxide were formed and allowed to burn to waste on the tops of the furnaces. The value of this gas as a fuel is now recognized, and it is consequently drawn off from the upper part of the furnaces and utilized for heating purposes.

**140. Temperature of Combustion.**—Although the absolute amount of heat evolved by the combustion of a unit weight of hydrogen, for instance, is always the same, yet the temperature produced may vary within certain limits. Thus, first of all, if within a given space, hydrogen is caused to burn in one instance at twice the rate of another, it follows that, as a greater number of units of heat are evolved in the same period of time, the temperature of that space will be raised proportionately higher. There are other causes that influence the temperature produced by combustion; for example, a jet of hydrogen, burning the same number of cubic feet per hour, produces a much higher temperature when it burns in oxygen than it does when burning in air (see Art. **35,** *Inorganic Chemistry*, Part 1).

If 2 grams of hydrogen are burned in oxygen, the heat

evolved has to raise the temperature of the 18 grams of water produced. But, if the oxygen is obtained from air, then not only have there to be heated the 16 grams of oxygen in the water produced, but also the 53.5 grams of nitrogen with which it (the oxygen) was mixed. The same number of units of heat are in the one case spread over 18 grams; in the other, over $18 + 53.5 = 71.5$ grams of gaseous matter—from which it follows that the temperature in the first instance must be very much higher than in the second.

**141. Structure of Flame.**—Flame may be defined as gaseous matter heated to the temperature at which it becomes visible, i. e., until it emits light. Solid particles begin, usually, to emit light when heated to about 500°, but gases, on account of their lower radiating power, must be raised to a much higher temperature, and hence the point of visibility is seldom attained, except by gases that are themselves combustible, and therefore capable of producing by their own combination with atmospheric oxygen the requisite degree of heat.

The presence of a combustible gas or vapor, therefore, is one of the conditions of the existence of the flame; a diamond or a piece of charcoal will burn in oxygen with a steady glow, but without flame, since the carbon is not capable of conversion into vapor, while sulphur, on the other hand, burns with a voluminous flame, in consequence of the facility with which it assumes the vaporous condition. It will be observed, moreover, that in the case of a non-volatile combustible the combination with oxygen is confined to the surface of contact, while in the flame of a gas or vapor the combustion extends to a considerable depth, the oxygen intermingling with the gaseous fuel.

Flames may be conveniently called *simple* or *compound*, according to the number of phenomena of combustion they involve; thus, for instance, the flames of hydrogen and carbon monoxide are simple, while those of marsh gas, olefiant gas, and hydrocarbons generally, are compound,

since they involve both the conversion of hydrogen into water and of carbon into carbon dioxide.

It is evident that simple flames, as a rule, must be hollow in ordinary cases, such as that of a gas issuing from a tube into the air, the hollow being occupied by the combustible gas to which the oxygen does not penetrate.

Most of the flames used are compound and involve several distinct phenomena. Before examining these more particularly, it seems advantageous to consider the conditions that regulate the luminosity of the flame.

In order that a flame may emit a brilliant light, it is essential that it should contain particles that, either from their own nature or from the conditions under which they are placed, do not admit of very much expansion by the heat of the flame, but are capable of being heated to incandescence. Thus, the flame of the oxyhydrogen blowpipe (see Art. **35,** *Inorganic Chemistry*, Part 1) emits a very pale light, but if the mixture of oxygen and hydrogen is restrained from expanding when fired, as in a eudiometer, it gives a bright flash; or if the flame is directed upon some solid body little affected by heat, such as lime, the light becomes extremely intense.

FIG. 27.

Phosphorus and arsenic burn with very luminous flames, in consequence of the formation of very dense vapors of phosphoric and arsenious oxides during the combustion, the density of the vapors being here attended with the same result as that produced by the restrained expansion of steam in the eudiometer.

It is not necessary that the incandescent matter should be a product of the combustion; any extraneous solid in a finely divided state will confer illuminating power to a flame. Thus, the flame of hydrogen may be rendered highly luminous by blowing a little very finely powdered charcoal into it by means of a bottle, as shown in Fig. 27.

The luminosity of all ordinary flames is due to the presence of highly heated carbon in a state of very minute division, and it remains to consider the changes by which this finely divided carbon is separated in the flame.

A candle, a lamp, and a gas burner exhibit contrivances for procuring light artificially in different degrees of complexity, the candle being the most complex of the three. When a candle is lighted, the first portion of the wick is burned away until the heat reaches that part which is saturated with the wax or tallow of which the candle is composed; this wax or tallow then undergoes destructive distillation, yielding a variety of products, among which olefiant gas is found in abundance. The flame furnished by the combustion of these products melts the fuel around the base of the wick, through which it then mounts by capillary attraction, to be decomposed in its turn and to furnish fresh gases for the maintenance of the flame. In a lamp, the fuel being liquid at the commencement, the process of fusion is dispensed with; and in a gas burner, where the fuel is supplied in a gaseous form, the process of destructive distillation has been already effected at a distance. It will be seen, however, that the final result is similar in all three cases, the flame being maintained by such gases as acetylene, marsh gas, and olefiant gas, arising from the destructive distillation of wax, tallow, oil, coal, etc., as the case may be.


FIG. 28.

The shape of the candle flame is common to all flames that consist of gas issuing from a small circular jet, like the wick of a candle. The gas issues from the jet in the form of a cylinder, which, however, immediately becomes a diverging cone by diffusing into the surrounding air. When this cone is kindled, the margin of it, where intermixture with the surrounding air is most complete, will be perfectly burned, but the gases in the interior of the diverging cone cannot burn until they have ascended

sufficiently to meet with fresh air; since these unburned gases are continually diminishing in quantity, the successive circles of combustion must diminish in diameter and the conical shape is the only possible form.

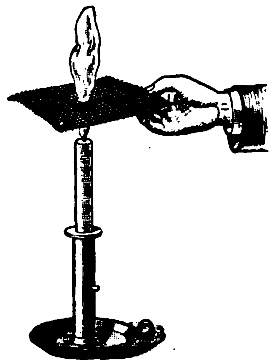

FIG. 29.

On examination of an ordinary flame—that of a candle, for example—it is seen to consist, as shown in Fig. 28, of three concentric cones, the innermost, around the wick, appearing almost black, the next emitting a bright white light, and the outermost being so pale as to be scarcely visible in broad daylight. There is also apparent a bright blue cup surrounding the base of the flame.

The dark innermost cone consists merely of the gaseous combustible to which air does not penetrate, and which, therefore, is not in a state of combustion.

The nature of this cone is easily shown by experiment. A piece of cardboard held across the flame near its base will not burn in the center where it traverses the innermost cone; a piece of wire gauze depressed upon the flame near the wick, as shown in Fig. 29, will allow the passage of the combustible gas, which may be kindled above it. The gas may be conveyed out of the flame by means of a glass tube, inserted into the innermost cone, and may be kindled at the other end of the tube, which, as shown in Fig. 30, should be inclined a little downwards. The combustible gas from the

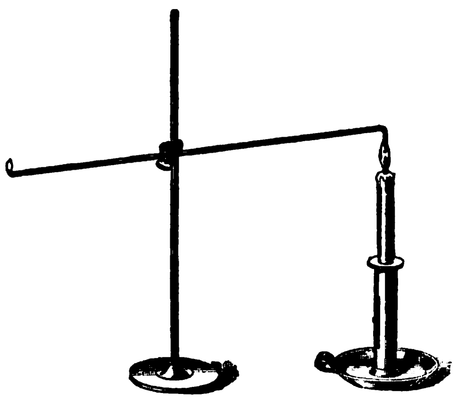

FIG. 30.

interior of a flame may be collected by using a flask, as shown in Fig. 31. This flask (*a* in the figure) is filled with water and furnished with two tubes, one of which *b* is drawn out to a point for insertion into the flame, while the other *c*, which runs down to the bottom of the flask, is bent as shown, and prolonged with a piece of rubber tubing so that it may act as a siphon. The flask is filled up with water, the jet *b* inserted into the interior of a flame, and the siphon set running by exhausting the tube *c* by suction. As the water flows out through the siphon, the gas is drawn into the flask, and, after the tube has been removed from the flame, the gas may be expelled by blowing down the siphon tube *c* and may be kindled at the jet *b*.

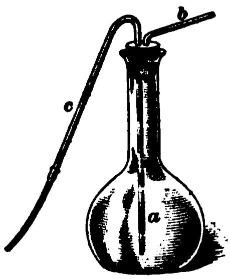

FIG. 31.

Should a candle be used for this experiment, it will always be found that some solid products of destructive distillation condense in the flask.

In the second, or luminous, cone, combustion is taking place, though it is not at all perfect, being attended by the separation of a quantity of carbon, which confers luminosity upon this part of the flame. The presence of free carbon is shown by depressing a porcelain disk or plate upon this cone, when a black film of soot will be found to have been deposited. The liberation of the carbon is due to the decomposition of the hydrocarbons by the heat, which separates the carbon from the hydrogen; and this latter, undergoing combustion, evolves sufficient heat to raise the separated carbon to a white heat, the supply of air that penetrates into this portion of the flame being insufficient to effect the combustion of the whole carbon.

It has been found experimentally that the temperature of the innermost cone of a hydrocarbon flame rises to about 1,000° near the apex of the cone. This temperature is sufficiently high to decompose the heavier hydrocarbons into acetylene. This acetylene is decomposed with the liberation

of carbon in the luminous cone, where the temperature rises to about 1,300°, owing to the combustion of the carbon monoxide and hydrogen, the former produced by the imperfect oxidation, and the latter by the decomposition of the hydrocarbons in the innermost cone.

A very simple experiment will clearly illustrate the nature of the luminous portion of the flame:

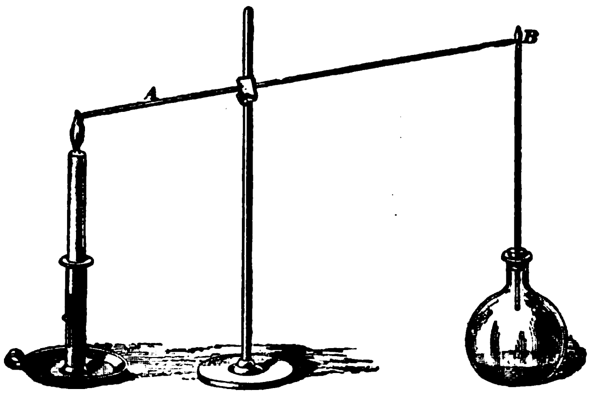


FIG. 32.

EXPERIMENT 32.—Over an ordinary candle flame a glass tube *A* is adjusted, as shown in Fig. 32, so as to convey the finely divided carbon from the luminous part of the flame into the flame of hydrogen *B*, which will thus be rendered as luminous as the candle flame, the dark color of the carbon being apparent in its passage through the glass tube.

The pale, outermost cone, sometimes called the *mantle* of the flame, in which the separated carbon is finally consumed, may be termed the *cone of perfect combustion*, and is much thinner than the luminous cone, the supply of air to this external shell of flame being practically unlimited, and the combustion therefore speedily effected.

The bright blue cup surrounding the base of the flame is formed by the perfect combustion (without any separation of carbon) of a small portion of the hydrocarbons, owing to the complete admixture of air at this point.

**142.** From this review of the structure of the flame, it is evident that, in order to secure a flame that shall be useful for illuminating purposes, attention must not only be paid to the composition of the fuel, but also to the supply of oxygen, or air, respectively.

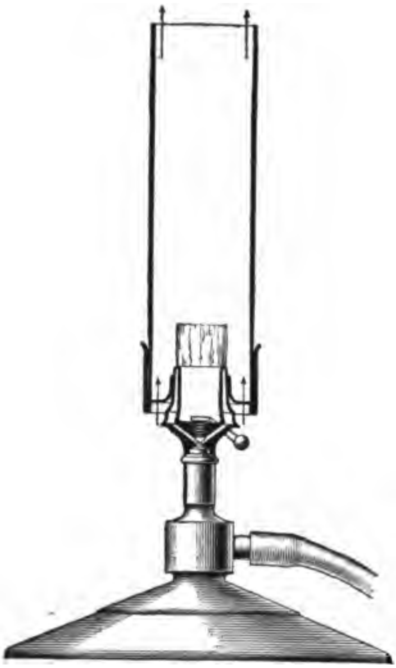

FIG. 33.

This latter necessity is accomplished in the burner proposed by Argand, now generally known as the *Argand burner.* In this burner, which is shown in Fig. 33, air is admitted into the gaseous center of the flame by making the flame ring-shaped. Moreover, by using a chimney to produce a draft, great brilliancy and steadiness of the flame are obtained.

For heating purposes, the best burner is *Bunsen's burner* (see Fig. 29, *Theoretical Chemistry*), in which the gas is conveyed through a narrow jet into a wide tube, at the base of which are two large holes for the admission of air. When a good supply of gas is turned on, a quantity of air, about twice the volume of the gas, is drawn in through the lower apertures; the mixture of air and gas may be kindled at the orifice of the wide tube, its rapid motion preventing the flame from passing down the tube. By closing the air holes, in turning the collar, a luminous flame is at once produced.

**143. Blowpipe Flame.**—The effect of converting a luminous flame into one devoid of light, but possessing considerable heating power, is also obtained by blowing a

current of air from a jet into the flame. The instrument used for this purpose is termed a *blowpipe*, and will be described at length in the analytic section of this course.

**144. The Miner's Safety Lamp.**—Davy discovered the fact that flame, if cooled below a certain point, is extinguished; hence, that no flame can be propagated through a cold, fine metal tube.

EXPERIMENT 33.—Wire gauze, being a collection of small, short tubes, will, consequently, not allow the passage of flame, and, when pressed upon a gas flame, will depress it in the same way as if it were a solid plate. If the gauze is held 2 inches above the jet, the gas may be lighted above the gauze, but the flame will not pass through to the jet. With two pieces of gauze, the gas may be made to burn between them, but neither above the upper nor below the lower; or, the gas may be made to burn above and below, but not between them.

The *miner's safety lamp*, generally known as *Davy's safety lamp*, is based on the facts of this discovery. It is represented in section in Fig. 34, and consists of a metallic lamp, the wick of which is surrounded with wire gauze, inclosed in a frame, by which the whole may be suspended. The explosive mixture of air with the gases developed in the mines can, of course, enter the gauze and burn within the gauze enclosure, but the flame cannot pass outwards through the gauze, since it is cooled, and consequently extinguished; hence, such a lamp prevents the explosion of these dangerous gases.


FIG. 34.

**145. Products of Combustion.**—The products of combustion may be divided into two classes; namely, the *physical products*, such as light and heat, for the sake of which combustion is generally produced; and the *chemical products* that are to be conveyed away.

The chemical products of combustion must be carbon dioxide and hydrogen oxide or water, since the combustibles are composed of carbon and hydrogen.

EXPERIMENT 34.—That water is one of the chemical products of combustion may be readily proved by holding a cold, and perfectly dry, bell glass over a candle flame; it will be noticed that it is at once bedewed with moisture. If, now, a little lime water is shaken up in the jar, it will become milky, thus proving the presence of carbon dioxide. The same is true of respiration; a full breath blown through a glass tube into lime water will make it entirely white.

**146. Ventilation.**—The air issuing from the lungs of a person at each expiration contains from 3.5 to 4 volumes of carbon dioxide in 100 volumes of air, and could not, therefore, be breathed again without danger. The total amount of carbon dioxide evolved by the lungs and skin amounts to about .7 cubic foot per hour. In order that it may be breathed again without inconvenience, this should be distributed through at least 140 cubic feet of fresh air, or a space measuring 5.2 feet each way. Hence the necessity for a constant supply of fresh air by ventilation, to dilute the carbon dioxide to such an extent that it may cease to impede respiration. This becomes the more necessary where an additional quantity of carbon dioxide is supplied by the burning of candles, gas, etc. An ordinary gas burner consumes at least 3 cubic feet of gas per hour, and produces about 1.7 cubic feet of carbon dioxide. Fortunately, a natural provision for ventilation exists in the fact that the processes of combustion and respiration, which contaminate the air, also raise its temperature, thus diminishing its specific gravity by expansion, and causing it to ascend and give, in this way, place for fresh air. Hence, the vitiated air always accumulates near the ceiling of an apartment, and it becomes necessary to afford it an outlet by opening the upper sash of the window.

The principles of ventilation are usually illustrated upon the lecturer's table by the following experiments and apparatus:

EXPERIMENT 35.—If a tall bell glass, closed at the top, is placed over a stand on which are three lighted candles at different heights, as

shown in Fig. 35, the heated carbon dioxide will accumulate in the upper part of the bell glass, and gradually extinguish the tapers from

FIG. 35.

FIG. 36.

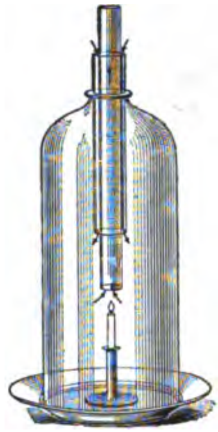

FIG. 37.

above downwards. By removing the stopper and raising the jar just before the last flame expires, the air is renewed and the taper will be revived.

EXPERIMENT 36.—If a wide glass tube is fixed in the neck of the bell glass, as shown in Fig. 36, and this is placed over a stand carrying two tapers, both will be extinguished, as in the previous experiment. But, if a small space is left between the bell glass and the plate, the upper taper only will be extinguished, while the lower one will be supplied with air from below, its carbon dioxide and water escaping through the tube.

EXPERIMENT 37.—If two large tubes, one within the other, are fixed in the neck of a bell glass in the way shown in Fig. 37, and the whole is placed over a candle flame, the heated products of combustion escape up the center tube, while fresh air enters through the space between the two tubes, and the candle will be found to burn actively.

Mines, as a rule, are ventilated by means of two shafts, called the *upcast* and the *downcast shaft*, respectively, their action being usually illustrated by the following experiment:

EXPERIMENT 38.—A square box *a*, shown in Fig. 38, has at each end a chimney, in one of which *b*, a candle is kept burning. The air heated

by the combustion rises, while fresh air descends in the opposite chimney *c* to supply its place.

Practically, a coal fire is kept burning at the base of the upcast shaft, and by suitably arranging doors in the different parts of the mine, the whole may be thoroughly ventilated. Should only one shaft be possible, an arrangement similar to the one illustrated in Experiment 39 is usually employed.

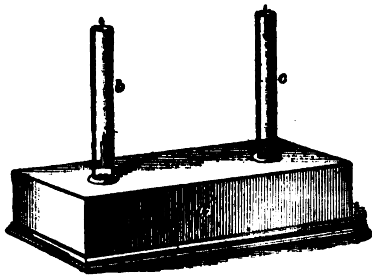


FIG. 88.

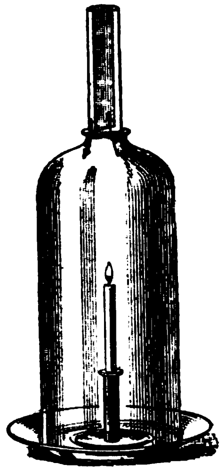

FIG. 89.

EXPERIMENT 39.—A candle is placed in a small bell glass, surmounted by a wide cylinder, as shown in Fig. 89. The candle will be seen to be extinguished very quickly. But, if a piece of tin plate is inserted in the tube, as shown in the illustration, the vitiated air will pass out on one side and fresh air will enter on the other; which is proved by the fact that the candle will now continue to burn.

## CARBON AND SULPHUR.

### CARBON DISULPHIDE.

*Formula $CS_2$. Density 37.965. Molecular weight 75.93. One liter of carbon disulphide vapor weighs 3.40 grams (37.965 criths).*

**147. History and Preparation.**—Carbon disulphide, sometimes called bisulphuret of carbon, was discovered by Lampadius in 1796. It is found in small quantities among

the products of destructive distillation of coal. It is one of the few compounds of carbon that can be obtained by the

FIG. 40.

direct union of their elements, and is always prepared synthetically by passing vapor of sulphur over charcoal heated to redness.

$$C_2 + 2S_2 = 2CS_2$$

EXPERIMENT 40.—In small quantities, carbon disulphide is easily prepared in a tube of German glass (a so called combustion tube) about

FIG. 41.

2 feet long and ½ inch in diameter. This tube is closed at one end, and enough small pieces of sulphur dropped into it to occupy about 2½ to 3 inches of the tube at the closed end. The rest of the tube is then filled up with small pieces of charcoal. The tube is placed in a combustion

furnace, and its open end connected, by means of a perforated cork, with a glass tube that dips just below the surface of the water contained in a bottle, which in its turn is placed in a vessel containing very cold water (ice water, preferably). The general arrangement of the apparatus is shown in Fig. 40.

The part of the tube that contains the charcoal is heated first; when this is red hot, the end containing the sulphur is heated so that the vapor of sulphur may be slowly passed over the red-hot charcoal. The disulphide being insoluble in water, and much heavier, having a specific gravity of 1.27, is deposited beneath the water in the receiver. To purify the carbon disulphide from the water and the excess of sulphur deposited with it, the water is carefully drawn off with a small siphon, the disulphide transferred to a flask, and a few pieces of calcium chloride dropped into it to absorb the water. A bent tube connected with a Liebig's condenser, or with a worm, is attached to the flask (see Fig. 41) by a perforated cork, and the flask is gently heated in a water bath, when the carbon disulphide is distilled over as a perfectly colorless liquid. Care should be taken, as carbon disulphide is easily inflammable.

**148. Properties.**—Carbon disulphide is a colorless, brilliant, and strongly refractive liquid which, when perfectly pure, possesses an agreeable ethereal odor, resembling that of chloroform. Its specific gravity is 1.27. It solidifies at $-116°$; and melts again at $-110°$; it boils at 46°, yielding a dense vapor. It is very volatile, evaporating rapidly in the air, producing great cold. It is readily inflammable, taking fire in the air at 150° and burning with a blue flame, producing carbon and sulphur dioxides by its decomposition. The vapor of carbon disulphide acts very injuriously if breathed for any length of time, its effects showing symptoms somewhat similar to those caused by hydrogen-sulphide poisoning.

Carbon disulphide has often been made the starting point in the attempts to produce organic compounds by synthesis. It may be employed in the formation of the hydrocarbons that are usually derived from organic sources; for, if it is mixed with hydrogen sulphide (by passing that gas through a bottle containing the disulphide gently warmed), and passed over copper filings heated to redness in a porcelain tube, olefiant gas will be produced according to the equation:

$$2CS_2 + 2H_2S + 6Cu = 6CuS + C_2H_4$$

The action of carbon disulphide on ammonia is practically important for the easy production of ammonium sulphocyanide, which is formed when the disulphide is dissolved in alcohol and acted on by ammonia with the aid of heat:

$$CS_2 + 2NH_3 = H_2S + NH_4CNS$$

**149. Uses.**—Carbon disulphide is used in the arts to dissolve phosphorus, iodine, and sulphur, the latter particularly in vulcanizing rubber. The chief application of carbon disulphide, however, depends on its power of dissolving oils and fats. After as much oil as possible has been extracted from seeds and fruits by pressure, a fresh quantity is obtained by treating the pressed cake with carbon disulphide, which is afterwards recovered by distillation from the oil. In Algiers, it is employed for extracting the essential oils that contain the perfumes of roses, lavender, jasmine, etc.

**150. Carbon monosulphide** $CS$ is deposited when $CS_2$ is exposed to sunlight, or left some weeks in contact with some iron wire:

$$2CS_2 + Fe = FeS_2 + 2CS$$

The $FeS_2$ (iron disulphide) is dissolved out by $HCl$, leaving the $CS$ as a red-brown powder having a specific gravity of 1.66, insoluble in alcohol and benzene, and slightly soluble in hot ether and $CS_2$. It is soluble in boiling nitric acid and boiling strong potash solution. At about 200°, it is converted into carbon and sulphur.

**151. Tricarbon disulphide** $C_3S_2$ has been obtained by boiling $CS_2$ in a flask, the upper portion of which contains an electric arc, and condensing the vapor, after it has thus been heated, so that it may fall back into the flask. It is a deep-red liquid of the specific gravity 1.27, and possesses a very irritating odor. When heated, it is transformed into a black mass.

**152. Carbon oxysulphide** $COS$ may be regarded as $CO_2$ in which an atom of $S$ has replaced an atom of $O$. It

is formed when a mixture of carbon monoxide with sulphur vapor is acted on by electric sparks, or is passed through a red-hot porcelain tube. It is more readily prepared by gently heating potassium sulphocyanide $KCNS$ with sulphuric acid, diluted with four-fifths of its volume of water, and collecting the gas over mercury. The action of the sulphuric acid on the potassium sulphocyanide produces hydrosulphocyanic acid:

$$KCNS + H_2SO_4 = HCNS + KHSO_4$$

which is then decomposed by the water, in the presence of the excess of sulphuric acid, into the carbon-oxysulphide gas and ammonia, which latter combines with the sulphuric acid:

$$HCNS + H_2O = NH_3 + COS$$

Carbon oxysulphide possesses a peculiar, disagreeable odor, closely resembling that of carbon disulphide; it is more than twice as heavy as air, its specific gravity being 2.10, and is very inflammable, burning with a blue flame, yielding carbon dioxide and sulphur dioxide.

Potash absorbs and decomposes it, yielding carbonate and sulphide of potassium; for instance,

$$COS + 4KOH = K_2S + K_2CO_3 + 2H_2O$$

## CARBON AND NITROGEN.

### CYANOGEN.

*Formula $C_2N_2$. Density 25.98. Molecular weight 51.96. The weight of 1 liter is 2.33 grams (25.98 criths).*

**153. History.**—Cyanogen was discovered by Gay-Lussac in 1815; being the first compound radical isolated, its discovery marks an era in the science of theoretical chemistry, and, to a still greater extent, in that of organic chemistry. Its name is derived from the Greek ***κύανος***, ***kyanos***, meaning "blue," in allusion to its being an important constituent

of the well known pigment, *Prussian blue*, then known as *prussiate of iron*, from which Gay-Lussac first obtained it.

**154. Preparation.**—Cyanogen can be obtained by heating the cyanide of gold, silver, or mercury:

$$Hg''(CN)_2 = Hg + (CN)_2$$

EXPERIMENT 41.—Instead of using the somewhat rare and rather expensive mercuric cyanide, a mixture of 2 parts of thoroughly dried potassium ferrocyanide and 3 parts of mercuric chloride may be used. The mixture is placed in a flask of hard glass upon a sand bath (see Fig. 42) and heated intensely by means of what is known, in laboratories, as the double-draft burner. The gas as it is evolved may be collected by displacement, its strong odor indicating when the jar is filled.

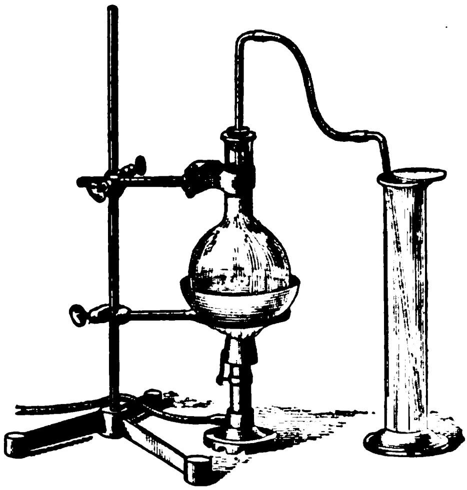

FIG. 42.

**155. Properties.**—Cyanogen is a colorless gas, possessing a strong odor of bitter almonds. Its specific gravity is 1.806. It may be easily condensed by a pressure of 4 atmospheres or at a temperature of −25° to a colorless, highly refractive liquid, which has a specific gravity of .866 and freezes at −34° to a transparent, ice-like solid. Water dissolves four and one-half times its own volume of cyanogen, and alcohol twenty times its own volume of the gas. On contact with flame, cyanogen readily takes fire, and burns with a characteristic pink flame edged with green, yielding carbon dioxide and nitrogen. The unsaturated group, *CN*, is sometimes written *Cy*.

Free, or molecular, cyanogen is composed of two of the

cyanogen radicals, $(CN)_2$ being analogous to $Cl_2$. Moreover, atomic cyanogen acts precisely like an elemental monad, forming compounds corresponding to the chlorides, thus:

| | | | |
|---|---|---|---|
| Potassium chloride | $KCl$ | Potassium cyanide | $KCN$ |
| Hydrochloric acid | $HCl$ | Hydrocyanic acid | $HCN$ |
| Hypochlorous acid | $HClO$ | Cyanic acid | $HCNO$ |

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## SILICON.

*Symbol Si. Atomic weight 28.* Valence IV. Specific gravity 2.49.*

**156. History and Occurrence.** — Silicon was first obtained pure by Berzelius in 1825. It does not occur free in nature, but is found abundantly in combination with oxygen, forming such well known substances as *quartz* and *flint*. In combination with oxygen, as well as with aluminum, potassium, and various other metals, it constitutes a large portion of the rock formations that make up the solid crust of the earth.

**157. Preparation and Properties.** — Silicon may be obtained by the action of sodium on potassium fluosilicate:

$$K_2SiF_6 + Na_4 = 2KF + 4NaF + Si$$

The silicon thus obtained is a brown powder (*amorphous silicon*), which resists the action of all acids, except hydrofluoric, by which it is decomposed, forming silicon fluoride and evolving hydrogen:

$$Si + 4HF = SiF_4 + 2H_2$$

It may also be dissolved by solution of potash, with the evolution of hydrogen, and the formation of potassium silicate. Though silicon burns brilliantly when heated in oxygen, it does not burn completely, owing to the fact that it

* The density and molecular weight of silicon are not known. The molecule is sometimes said to contain 2 atoms, but this has not been determined with certainty.

becomes coated with silicic oxide, which is fused by the intense heat of the combustion. When heated with the blow-pipe on platinum foil, it eats a hole through the metal, with which it forms the fusible platinum silicide.

If potassium fluosilicate is fused with aluminum, a portion of the latter combines with the fluorine, while the remainder combines with the silicon, forming aluminum silicide. By boiling this with hydrochloric acid and then with hydrofluoric acid, the aluminum is extracted, and crystalline scales of silicon, possessing a metallic luster, resembling that of black lead, are left. These crystalline scales are known as *graphitoid silicon*. In this shape, silicon does not burn in oxygen, nor is it then soluble in hydrofluoric acid; a mixture of nitric and hydrofluoric acid, however, is capable of dissolving it. Though amorphous silicon is a non-conductor of electricity, the crystalline variety, like graphite, readily conducts it. The amorphous variety may, through an extremely intense heat, be transformed into the incombustible and insoluble form. It seems appropriate to remark that the combustibility of amorphous carbon (charcoal) is also diminished to a considerable extent after exposure to a high temperature.

Silicon is capable of being fused at a temperature somewhat above the melting point of cast iron; on cooling, it forms a brilliant metallic-looking mass, which may be obtained by certain processes, crystallized in octahedrons, whose hardness is so great that they scratch glass like diamond.

In their chemical relations to other substances, a considerable analogy exists between silicon and carbon. Silicon, however, is capable of displacing carbon; as, for instance, if potassium carbonate is fused with silicon, the former is dissolved, forming potassium silicate, and carbon is separated. Silicon further resembles carbon in its disposition to unite with metals, and to form compounds that retain their metallic luster; it unites directly with zinc, platinum, and aluminum, forming compounds that resemble metallic alloys. Nitrogen enters into combination with silicon directly at high temperature.

## SILICON AND HYDROGEN.

### HYDROGEN SILICIDE.

*Formula $H_4Si$. Molecular weight 32.*

**158. History and Preparation.**—This compound was discovered by Wöhler and Buff in 1857, and obtained in a pure state in 1867 by Friedel and Ladenburg. It is generally prepared by decomposing magnesium silicide by hydrochloric acid:

$$Mg_2Si + 4HCl = 2MgCl_2 + H_4Si$$

EXPERIMENT 42.—The first step in this experiment is to prepare magnesium silicide. For this purpose 40 parts of fused magnesium chloride, 35 parts of dried sodium fluosilicate, 10 parts of sodium chloride, and


FIG. 43.

20 parts of sodium cut in small pieces, are thoroughly mixed together and thrown into a red-hot Hessian crucible, which, after being covered with a lid, is further heated until the sodium ceases to burn. When cold, a dark layer of the impure silicide will be found at the bottom; this is detached and may be preserved in a small, tightly corked bottle.

To prepare, now, hydrogen silicide, the coarsely pulverized slag is placed in a wide-mouthed bottle $A$, Fig. 43, through the cork of which passes a funnel tube $B$ to the bottom of the bottle, and a wide delivery tube $C$, for the escape of the gas. The bottle is then filled with cold water, which, however, must have been recently boiled in order to expel its air, and placed by the pneumatic trough, as shown in the illustration. Upon pouring concentrated hydrochloric acid down the

funnel, being very careful that it does not carry any air bubbles with it, hydrogen-silicide gas is evolved and may be collected for use.

**159. Properties.**—Hydrogen silicide is a colorless gas, which at $-5°$ under a pressure of 70 atmospheres is condensed into a liquid. It is insoluble in water. When mixed with hydrogen, it is spontaneously inflammable in air, yielding white clouds of silicic oxide. Burned from a jet, the gas gives a brilliant white flame, which deposits a layer of brown silicon upon a disk or plate of porcelain held in it. When the tube conveying the gas is heated, a mirror-like deposit of silicon is formed within the tube. Passed into cupric sulphate or silver nitrate, it precipitates cupric and silver silicide, respectively.

Its composition can be easily proved by decomposing it with potassium hydroxide:

$$SiH_4 + 4KHO = K_4SiO_4 + 4H_2$$

It is readily seen from the equation that 1 volume of the gas with potassium hydroxide yields 4 volumes of hydrogen, and that one-half of this hydrogen comes from the silicide; each molecule must then contain 2 molecules of hydrogen, or 4 atoms.

## SILICON AND OXYGEN.

### SILICIC OXIDE.

*Formula $SiO_2$. Molecular weight 59.92.*

**160. Occurrence.**—Silicic oxide, which is better known under the name of *silica*, occurs widely distributed in nature. Its purest natural form is a transparent and colorless variety of quartz known as *rock crystal*, which is often seen crystallized in beautiful six-sided prisms, terminated by six-sided pyramids as shown in Fig. 44, and which are always easily recognized by their great hardness, scratching glass almost as readily as the diamond. Colored a delicate purple, presumably by a little organic matter, these crystals are known as *amethysts;*

FIG. 44.

when of a brown color, they are known as *cairngorm stone*, or *Scotch pebbles*. Losing its transparency and crystalline structure, silica is met with in the form of *chalcedony* and of *carnelian*, usually colored in the latter with oxide of iron. We further find it constituting such precious stones as *agate*, *jasper*, *cat's eye*, *opal*, *onyx*, etc.

Sand, of which the white varieties are nearly pure silica, appears to have been formed by the disintegration of silicious rocks, and has very often a red or yellow color, owing to the presence of iron oxide.

Flint consists essentially of silica colored with various impurities. Flints are generally found in compact masses, distributed in regular beds throughout the chalk formation.

The part taken by silica in natural operations appears to be chiefly a mechanical one, for which its stability under ordinary influences peculiarly fits it, and is found to constitute the great bulk of the soil which serves as a support and food reservoir for land plants, and enters largely into the composition of the greater number of rocks.

That silica, however, is not entirely excluded from any share in life is proved by its presence in the shining outer sheath of the stems of certain plants; as, for instance, in the joints of the bamboo, where it forms the greater part of the matter known as *tabasheer*, and in the hard external coating of a plant known as *Dutch rush*. These facts alone would lead naturally to the inference that silica could not be absolutely insoluble, since the capillary vessels of plants are known to be capable of absorbing only such substances as are in a state of solution. Many natural waters also show that they contain silica in a dissolved state, and frequently in considerable quantity too, as, for instance, in the geysers in Iceland, which deposit a coating of silica upon the earth around their borders.

**161. Preparation.**—Silica may be prepared either by the oxidation of silicon, as when it burns in the air, or by the dehydration of silicic acid:

$$H_2SiO_3 - H_2O = SiO_2$$

**162. Properties.**—Silicic oxide, in the form in which it is usually obtained, is a white amorphous powder, though in nature it occurs frequently, as has been previously mentioned, in the form of hexagonal prisms. It has a specific gravity of 2.60, is so hard as to scratch glass, and is fusible only by means of an oxyhydrogen blowpipe. The natural varieties of silica are not soluble in pure water, the action of an alkali being required to bring it into a soluble form.

In order to effect this upon a small scale, some white sand is finely powdered in an agate mortar, mixed with about four times its weight of dried sodium carbonate, placed upon a piece of platinum foil, the edges of which are slightly bent upwards, and fused by directing the flame of a blowpipe upon the under side of the foil. Effervescence will soon be observed, due to the escape of carbon dioxide. The piece of platinum foil, when cool, may be placed in a little warm water, and allowed to soak for some time, when the melted mass will gradually dissolve, forming a solution of *sodium silicate*. This solution will be found decidedly alkaline to test paper.

If a portion of the solution of sodium silicate in water is poured into a test tube, and two or three drops of hydrochloric acid are added to it, with occasional agitation, effervescence will be produced by the expulsion of any carbon dioxide still remaining, and the solution will be converted into a gelatinous mass by the separation of silicic acid. But, if another portion of the solution is poured into an excess of dilute hydrochloric acid (i. e., into enough to render the solution distinctly acid), the silicic acid will remain dissolved in the water, together with the sodium chloride formed. In order to separate the sodium chloride from the silicic acid, the process of dialysis must be resorted to.

**Dialysis** (from the Greek διαλύειν, *dialuein*, meaning "to part asunder") may be defined as the separation of dissolved substances from one another by taking advantage of the different rates at which they pass through moist *diaphragms*, or *septa*. Those substances that crystallize (*crystalloids*), it has been found, as well as the mineral acids, pass through

such septa in solution faster than amorphous substances (*colloids*).

If a mixed solution of sodium chloride and silicic acid were poured upon an ordinary paper filter, it would pass through without any alteration; but, if parchment paper is employed, which is not pervious to water, although readily moistened by it, none of the liquid will pass through. If the cone of parchment paper be supported upon a vessel filled with water, as shown in Fig. 45, so that the water may be in contact with the outer surface of the cone, the hydrochloric acid and sodium chloride will pass through the substance of the parchment paper, and the water charged with them may be seen descending in dense streams from the outside of the cone. After a few hours, especially if the water is changed occasionally, the whole hydrochloric acid and sodium chloride will have passed through, and a pure solution of silicic acid in water will remain in the cone.

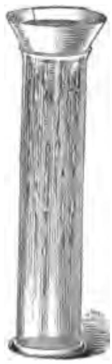

FIG. 45.

A convenient form of dialyzer, met in most laboratories, is shown in Fig. 46; it consists of parchment paper stretched over a hard rubber ring and held in this position by a concentric ring. It is suspended on a surface of water and the solution to be dialyzed is poured upon it.

FIG. 46.

This solution is believed to contain the *orthosilicic acid* $H_4SiO_4$. It is very feebly acid to blue litmus paper, and possesses no perceptible sour taste. It has a great tendency to form into a jelly, in consequence of the sudden separation of silicic acid. If it is slowly evaporated in a dish, it soon solidifies; but, by conducting the evaporation in a flask, so as to prevent any drying of the silicic acid at the edges of the liquid, it may be concentrated until it contains 14 per cent. of silicic acid. When this solution is kept, even in a stoppered bottle, it soon sets into a

transparent, gelatinous mass, which gradually shrinks and separates from the water. When evaporated in vacuo over sulphuric acid, it gives a transparent, lustrous glass, which is composed of 22 per cent. of water and 78 per cent. of silica $H_2OSiO_2$, which is also the composition of the gelatinous precipitate produced by acids in the solution of sodium silicate. It is called *metasilicic acid*, whose formula is $H_2SiO_3$, or $SiO(HO)_2$, as it is sometimes written.

Silica in the natural crystallized form, as rock crystal and quartz, is insoluble in boiling solutions of the alkalies, as well as in all acids, except hydrofluoric acid; but amorphous silica (such as opal and tripoli) is readily dissolved in boiling alkalies. These represent, in fact, two distinct modifications of silica, which may be said to be dimorphous. A transparent piece of rock crystal may be heated to bright redness without change; but, if it is powdered previously to being heated, its specific gravity is diminished from 2.6 to 2.4, and it becomes soluble in boiling alkalies, having been converted into the amorphous modification. The natural forms of amorphous silica of specific gravity 2.2 are always hydrated, and even some of the varieties of specific gravity 2.6, such as flint, agate, and chalcedony, contain a little water, pointing to the aqueous origin of all silica.

Crystals of quarts have been obtained artificially by the prolonged action of water on glass under pressure. When fused with the oxyhydrogen blowpipe, silica does not crystallize, being thus converted into the amorphous variety of specific gravity 2.2. Quartz is a good insulator of electricity, far surpassing glass in a moist atmosphere.

**163. Silicates.**—The acid properties of silicic acid are so feeble that it is a matter of great difficulty to determine the proportion of any base required to react with it in order to form a chemical neutral salt. Like carbonic acid, it does not destroy the action of the alkalies on test papers, and we are therefore deprived of this method of ascertaining the proportion of alkali that neutralizes it in a chemical sense. In attempting to ascertain the quantity of alkali with which

silica combines, from that of the carbon dioxide, which it expels when heated with an alkaline carbonate, it is found that the proportion of carbon dioxide varies considerably, according to the temperature and the proportion of alkaline carbonate employed.

By heating silica with sodium hydroxide $NaOH$ it is found that 60 parts of silica expel 36 parts of water, however much $NaOH$ is employed; and the same proportion of water is expelled from barium hydroxide $(BaOH)_2$ when heated with silica.

The formula $SiO_2$ represents 60 parts by weight of silica, and 36 parts represent 2 molecules of water. Hence, it would appear that the action of silica on sodium hydroxide is represented by the equation

$$4NaOH + SiO_2 = Na_4SiO_4 + 2H_2O$$

and that on barium hydroxide by the equation

$$2Ba(OH)_2 + SiO_2 = Ba_2SiO_4 + 2H_2O$$

and since it is found that several of the crystallized mineral silicates contain a quantity of a metal equivalent to $H_4$, it is customary and justifiable to represent silicic acid as a tetrabasic acid $H_4SiO_4$, containing 4 atoms of hydrogen, which may be replaced by metals.

The feebly acid character of $SiO_2$ will recall that of $CO_2$. Other comparisons, however, between these two analogous compounds are hardly possible, on account of their different physical conditions.

The silicates form by far the greatest number of minerals. The different varieties of clay consist of aluminum silicate; feldspar is a silicate of aluminum and potassium, meerschaum a silicate of magnesium, etc.

The different kinds of glasses are composed of silicates of potassium, sodium, calcium, lead, etc. None but the silicates of the alkali metals are soluble in water.

Scarcely any of the silicates are represented by formulas that express their derivation from the acid $H_4SiO_4$; they are generally represented as derivatives of metasilicic acid and of polysilicic acids, i. e., compounds of $nH_2O$

with $SiO_2$ (*n* standing for the varying number of $H_2O$ molecules).

This tendency of silicon to form complex mineral compounds is comparable with that of its analogue, carbon, to form complex organic compounds; but, while oxygen is the other element mostly concerned in the formation of mineral silicates, hydrogen is the predominant companion of carbon in organic derivatives.

**164. Uses of Silica.**—Silica is largely employed in all its various forms. Rock crystal is used for the manufacture of ornaments, spectacle glasses, and lenses. Chalcedony, onyx, and opal are sought for by the engraver and lapidary. Agate, which is very hard, is used for the manufacture of mortars, etc. Sandstone serves for building purposes and for grindstones ; sand, for mortars, the manufacture of glass, pottery, etc.

## SILICON AND CHLORINE.

### SILICON CHLORIDE.

*Formula* $SiCl_4$. *Molecular weight 169.48.*

**165. Preparation.**—This compound is formed when silicon is heated to dull redness in a current of chlorine, or when the latter gas is passed over an incandescent mixture of charcoal and silica, according to the equation:

$$SiO_2 + C_2 + 2Cl_2 = SiCl_4 + 2CO$$

Silica, lampblack, and oil are thoroughly mixed into a stiff paste. This paste is made into little balls, which are placed in a crucible, the cover of which is then luted, and the whole is heated to redness in a furnace. When cool, the balls are introduced into a porcelain tube or a clay retort, which is heated to bright redness in a furnace, while a current of carefully dried chlorine is passed through. The silicon chloride and the carbon monoxide formed are passed through

two **U** tubes surrounded by a freezing mixture. By this means the silicon chloride is condensed.

**166. Properties.**—Silicon chloride, or silicon tetrachloride, is a colorless, heavy liquid, specific gravity 1.52, and is volatile. Its boiling point is 59° and it fumes readily when exposed to air, the moisture of which decomposes it, yielding hydrochloric acid and silicic acid, according to the equation:

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl$$

**167.** When silicon is heated with hydrogen chloride, a compound—which, from its similarity in constitution to chloroform $CHCl_3$, has obtained the name *silicochloroform* $SiHCl_3$—is formed according to the equation:

$$Si + 3HCl = SiHCl_3 + H_2$$

This compound is a colorless, strong-smelling liquid, which boils at 38°, and, unlike most chlorine compounds (including pure chloroform), is inflammable, burning with a greenish flame and producing $SiO_2 + HCl$.

**168. Silicon Trichloride** $Si_2Cl_6$.—This compound, which is also known as *silicon hexachloride*, is formed when silicon chloride is passed over silicon heated to whiteness in a porcelain tube. It is a colorless liquid, specific gravity 1.58, solidifying at − 1° and boiling at 146°. The specific gravity of its vapor is 9.7. It fumes strongly in the air, and takes fire when heated.

## SILICON AND IODINE AND BROMINE.

**169.** With bromine and iodine, silicon forms also the compounds $SiBr_4$, $Si_2Br_6$, $SiI_4$, and $Si_2I_6$, which are analogous in composition to the chlorine compounds.

$SiBr_4$ (*tetrabromide of silicon*) is a colorless, heavy liquid, which boils at 154° and solidifies to a crystalline mass at 13°. $Si_2Br_6$ (*silicon tribromide*) forms large crystalline tablets, melts when heated, and distils without decomposition at 240°.

$SiI_4$ (*tetraiodide of silicon*) is obtained by direct combination. It melts at 120.5° and boils at 290°. It takes fire when heated in the air and burns with a reddish flame. It is decomposed by water into hydriodic and silicic acids. $Si_2I_6$ (*silicon triiodide*) is obtained when tetraiodide of silicon is heated at 280° with finely divided silver. It crystallizes from carbon disulphide in beautiful, colorless, hexagonal prisms or rhombohedrons, which, on exposure to moist air, are converted into a white mass, with the formation of silicic and hydriodic acids. Subjected to heat, silicon triiodide melts and is reduced to a lower iodide, probably $Si_2I_4$. Ice-cold water decomposes it, with the formation of a white substance $Si_2O_4H_2$, known as *silico-oxalic acid*, the name being given from its analogy to oxalic acid $C_2O_4H_2$. This compound is decomposed by weak bases into hydrogen and silica. $SiHI_3$, which is formed on passing a mixture of hydrogen and hydriodic acid over silicon heated to low redness, is a strongly refracting, colorless liquid. Like silicochloroform, it is decomposed by water.

## SILICON AND FLUORINE.

### SILICON TETRAFLUORIDE.

*Formula* $SiF_4$. *Molecular weight 104.*

**170.** On heating a mixture of powdered fluorspar and glass with concentrated sulphuric acid in a small flask, a gas is evolved that possesses a very pungent odor and produces thick white fumes on coming in contact with the atmospheric air. This gas is silicon tetrafluoride, and may be represented as silica in which the oxygen has been displaced by fluorine. The changes of place between these two elements in the above experiment is represented by the following equation:

$$\underset{\text{fluorspar}}{2CaF_2} + \underset{\text{silica (glass)}}{SiO_2} + \underset{\text{sulphuric acid}}{2H_2SO_4} = \underset{\text{calcium sulphate}}{2CaSO_4} + \underset{\text{silicon tetra-fluoride}}{SiF_4} + \underset{\text{water}}{2H_2O}$$

This gas might at first be mistaken for hydrofluoric acid; but, if a moistened glass rod is exposed to the gas, the wetted surface quickly becomes coated with a white film, which proves on examination to be silica. This formation of the crust of silica on the wetted surface is due to a decomposition that takes place between the tetrafluoride and the water, in which the oxygen and fluorine again change places, as shown in the subjoined equation:

$$SiF_4 + 2H_2O = SiO_2 + 4HF^*$$

Since this latter equation shows that hydrofluoric acid is again formed, it would be expected that the glass beneath the deposit of silica would be found corroded by the acid. This, however, is not the case, and when the experiment is repeated on a somewhat larger scale, so that the water that has acted on the gas may be examined, it will be found to hold in solution, not hydrofluoric acid, but an acid that has only a very little action on glass, and is composed of hydrofluoric acid and silicon fluoride. The hydrofluoric acid, produced when water acts on the fluoride, combines, therefore, with a portion of the latter to produce the new acid, hydrofluosilicic acid $(HF)_2SiF_4$, or $H_2SiF_6$.

Silicon tetrafluoride is a colorless, pungent gas, which condenses to a colorless liquid under a pressure of 30 atmospheres, or when cooled to $-107°$, and solidifies at $-140°$.

**171. Hydrofluosilicic Acid** $H_2SiF_6$.—This acid is obtained in solution by passing silicon tetrafluoride into water:

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$$

The gas must not be passed directly into the water, as the

*The student will notice that the proportion of $SiF_4$ to $H_2O$ in this equation, which represents the decomposition of the gas by water, is the same as that in the preceding equation, representing the evolution of the gas together with water, so that the equations apparently contradict each other. In reality, it depends on the actual masses of water and other substances present, and also on the temperature, whether $SiF_4$ and $H_2O$ can exist together or will at once decompose each other. The excess of sulphuric acid used in the preparation of $SiF_4$ will combine with the water, and will prevent it from decomposing the $SiF_4$.

separated silica would stop the opening of the tube; in order to prevent this, the delivery tube should dip into a little mercury at the bottom of the water, when each bubble, as it rises through the mercury into the water, will become surrounded with an envelope of gelatinous silica; and, if the bubbles are evolved fairly regular, they may even form a tube of silica extending through the whole height of the water. To obtain the acid, the thick jelly is pressed through a linen filter, and the filtrate is evaporated at a low temperature. The saturated solution is a fuming and strongly acid liquid, which on boiling decomposes into silicon fluoride and hydrofluoric acid; as this solution corrodes glass and porcelain when evaporated in them, a platinum dish must be used for this purpose. If the solution of hydrofluosilicic acid is neutralized with potash and stirred, a very characteristic crystalline precipitate of *potassium silicofluoride* (*potassium fluosilicate*) is formed:

$$H_2SiF_6 + 2KOH = \underset{\substack{\text{potassium}\\\text{silicofluoride}}}{K_2SiF_6} + 2H_2O$$

But, if an excess of potash is employed, a precipitate of gelatinous silica will be separated, potassium fluoride remaining in the solution:

$$H_2SiF_6 + 6KOH = 6KF + 4H_2O + SiO_2$$

One of the chief uses of hydrofluosilicic acid is to separate the potassium from its combination with certain acids, in order to obtain these in the separate state.

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## SILICON AND SULPHUR.

**172. Silicon disulphide** $SiS_2$ is obtained by passing the vapor of carbon disulphide over a strongly heated mixture of silica and carbon. It forms long, silky needles, which are decomposed by water, yielding hydrogen sulphide and silica. The *monosulphide* $SiS$, and an *oxysulphide*, having probably the composition $SiSO$, are formed, together with other products, when sulphur vapor is passed over silicon

heated to whiteness in a combustion tube. The $SiS$ is yellow and the $SiSO$ is yellowish; both are volatile and condense on the cooler, but still hot, part of the tube.

**173. Silicon chlorihydrosulphide** $SiCl_3SH$ is formed when a mixture of vapor of silicon tetrachloride and hydrogen sulphide are passed together through a red-hot tube, according to the equation:

$$SiCl_4 + H_2S = HCl + SiCl_3SH$$

It is a colorless, fuming liquid, and boils at 96°.

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## SILICON AND NITROGEN.

**174. Silicon nitride** $SiN$ has been obtained by heating silica with carbon in a blast furnace, and treating the products successively with hydrofluoric acid and potash, when the nitride is left as a green infusible powder, which is attacked by potash at red heat, yielding potassium silicate, hydrogen, and ammonia. $Si_3N_4$ is formed by heating silicon in nitrogen.

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## SILICON AND CARBON.

**175. Silicon Carbide.**—As elements that are closely related show very little tendency to combine with one another, carbon and silicon will unite only when submitted to a very high temperature. When, however, silicon or silica and carbon are heated together in the electric furnace, they unite, forming silicon carbide $SiC$, commonly called carborundum; and by treating the mass first with nitric and hydrofluoric acids and then with nitric acid and potassium chlorate, it is obtained in colorless, transparent, tabular crystals, whose specific gravity is 3.12. Being nearly as hard as diamond, it has been proposed as a polishing material. It burns very slowly in oxygen when finely divided and strongly heated. Most oxidizing agents do not attack it even when fused with it, though a melted alkali converts it into carbonate and silicate of the alkali metal.

**176.** When cast iron containing silicon is boiled with hydrochloric acid until the whole of the iron is dissolved, a gray, frothy residue is left. If this be collected on a filter, and well washed and dried, it is found to consist of black scales of graphite, mixed with a very light white powder. On boiling it with potash, hydrogen is evolved and the white powder dissolves, forming a solution containing potassium silicate. This white powder appears to be identical with a substance obtained by other processes and called *leucone* (derived from the Greek λευκός, *leukos*, meaning "white"), which is believed to have the composition $Si_2H_2O_3$, or $O(SiOH)_2$. Its action on a solution of potash would be explained by the equation:

$$Si_2H_2O_3 + 4KOH = 2K_2SiO_3 + H_2O + 2H_2$$

Leucone is slowly converted into silicic acid, even by the action of water, hydrogen being disengaged. It burns when heated in air.

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## BORON.

*Symbol B. Atomic weight 11.* Valence III. Specific gravity 2.68.*

**177. History and Occurrence.**—Closely allied in various respects to silicon is another element, boron, which is almost entirely confined to the mineral kingdom; it has, however, lately been found in grape vines and in a few other plants.

Under the Arabic name *buraq* (corrupted into borax), a salt, obtained from certain lakes in Thibet, which contains boron as an essential constituent, has been imported into Europe for a long time, and has been used in medicine, in working metals, and in imitating precious stones.

From this borax, in 1702, Homberg obtained boric oxide, and, from boric oxide, Davy, in 1807, by utilizing electricity, and Gay-Lussac and Thenard, in 1808, by chemical processes,

* The density and molecular weight of boron are unknown.

obtained pure boron. Wöhler and Deville succeeded, 1856, in crystallizing it. The mineral *sassolite* is *boric acid* $H_3BO_3$; and *borax*, *boracite*, and *larderellite* are native borates of sodium, magnesium, and ammonium, respectively.

**178. Preparation and Properties.**—Boron possesses two distinct forms: amorphous and crystalline. Amorphous boron may be prepared by the action of sodium upon potassium fluoborate, according to the equation:

$$2KBF_4 + 6Na = 2KF + 6NaF + B_2$$

The boron thus obtained is a greenish-brown powder, of specific gravity 2.45, which burns with a green flame at 700° and is a rather poor conductor of electricity. It is readily oxidized by nitric acid and is fusible at the heat of the oxyhydrogen flame.

It may be obtained crystallized by very strongly heating amorphous boron with aluminum, and afterwards extracting the aluminum from the mass with hydrochloric acid; but these crystals are seldom pure, as they are found to contain mostly traces of aluminum and carbon. These crystals are short quadratic octahedrons (specific gravity 2.68), which not only vary from honey yellow to garnet red in color, but are also sometimes obtained nearly colorless. They closely resemble the diamond in their refractive power and in their hardness, which is so great that they will scratch rubies and will even wear away the surface of the diamond. These crystals are infusible; they cannot be attacked by any acid, and are only combustible with difficulty, even in oxygen. The so called *graphitoidal boron* is a compound of boron and aluminum.

Boron burns when heated at 410° in chlorine, forming boron trichloride. It forms a compound with hydrogen, which has, however, never been obtained free from admixed hydrogen, but which probably has the formula $BH_3$. This compound is an inflammable gas, burning with a green flame, and is obtained by heating fused boric oxide $B_2O_3$ with magnesium, and treating the mass with hydrochloric acid. Boron

absorbs nitrogen much more readily than silicon, when heated to redness, forming a white, infusible, insoluble powder—boron nitride $BN$.

Notwithstanding the many points of similarity between boron, carbon, and silicon, boron cannot very well be considered as belonging to the same family of elements as that which includes carbon and silicon, because, while $C$ and $Si$ are tetravalent elements, boron is trivalent and should, therefore, be classed more properly with phosphorus and nitrogen.

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## HALOGEN COMPOUNDS OF BORON.

**179. Boron chloride** $BCl_3$ may be obtained by heating crude amorphous boron in a current of chlorine, or by passing dry chlorine over a strongly heated mixture of boric oxide and charcoal, according to the subjoined equation:

$$B_2O_3+3C+3Cl_2 = 2BCl_3+3CO$$

In a pure state, boron chloride is a colorless and highly refractive liquid of specific gravity 1.35 at 17°, which boils at 18.23° and fumes in the air. It is readily decomposed by water into boric and hydrochloric acids:

$$BCl_3+3H_2O = 3HCl+B(OH)_3$$

**180. Boron bromide** $BBr_3$ is obtained either by direct combination of its constituents or by passing bromide vapor over a heated mixture of charcoal and boric oxide. It is a strongly fuming, colorless liquid, specific gravity 2.69, which boils at about 90°.

**181. Boron fluoride** $BF_3$ was discovered by Gay-Lussac and Thenard in 1810. It is prepared by heating in a glass retort an intimate mixture of 1 part of boric oxide and 2 parts of finely powdered calcium fluoride with 12 parts of sulphuric acid. The gas evolved is collected over mercury. The occurring reaction may be expressed by the following equation:

$$3CaF_2+B_2O_3+3H_2SO_4 = 3CaSO_4+3H_2O+2BF_3$$

Boron fluoride is a colorless gas, having an extremely suffocating odor; it is decomposed by water, and must, therefore, as has been already mentioned, be collected over mercury. Its affinity for water is so great that it carbonizes paper and certain organic substances, in the same way as does strong sulphuric acid. Potassium and sodium burn brilliantly when heated in the gas.

The solution of boron fluoride in water is accompanied by a chemical reaction, which is shown when the aqueous solution of this gas, saturated at ordinary temperatures, is cooled to 0°; for crystals of boric acid are deposited, and a very acid liquid, *hydrofluoboric acid* $HBF_4$, formed, according to the equation:

$$8BF_3 + 6H_2O = 6HBF_4 + 2B(OH)_3$$

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## BORON AND OXYGEN.

**182. Boric oxide** $B_2O_3$ is formed whenever boron burns in air or oxygen. It is usually obtained by igniting its hydrate, boric acid $B(OH)_3$. A viscid mass is left, which solidifies to a colorless, transparent, and brittle glass having a specific gravity of 1.83.

**183. Boric acid** $B(OH)_3$ or $O_3BH_3$ was discovered by Homberg in 1702. It occurs free in nature in volcanic districts, as in Tuscany, where it issues, mixed with steam and gaseous matter, from fissures in the earth into natural or artificial little lakes or ponds, known as *lagoons*, or *lagoni*. The gases (*suffioni*) contain sensible traces of boric acid, which is dissolved by the water of the lagoni, which soon becomes charged with the acid. On evaporation this water furnishes the crude boric acid. Boric acid may be prepared from sodium borate or borax, by dissolving 3 parts of it in 12 parts of boiling water, adding 1 part of sulphuric acid, and allowing the whole to cool. The boric acid separates out in white, crystalline scales of specific gravity 1.48 and which are somewhat greasy to the touch. They are soluble in 2½ parts

of water at 18°, and freely soluble in alcohol, the latter solution burning with a greenish flame. The aqueous solution of boric acid is feebly acid; it changes blue-litmus solution to a wine color and turns turmeric paper brown. This constitutes the *normal* or *orthoboric* acid. When heated to 120°, it loses 1 molecule of water and is converted into *metaboric acid* $HBO_2$. If the latter is maintained for some time at a temperature of 140°, it is converted into tetraboric acid $H_2B_4O_7$ according to the equation:

$$4HBO_2 = H_2B_4O_7 + H_2O$$

Boric acid shows a strong tendency to condensation, thus forming multiple salts. *Borax*, or *sodium tetraborate* $Na_2B_4O_7$, is an example. Borax is found native in the waters of certain lakes in Thibet and in the waters of Borax Lake and Lake Clear, about 250 miles north of San Francisco, California. It is used largely as a flux in working metals.

# INORGANIC CHEMISTRY.

(PART 3.)

## GENERAL PRINCIPLES.

### ATOMS AND MOLECULES.

**1.** It is only after numerous facts have been observed and accurately described that it is possible to deduce such general principles as will enable the student to conduct his future work and experiments in such a manner that he may proceed advantageously to himself with the smallest possible expenditure of time and energy.

Numerous statements made in the following pages will be thoroughly familiar to the student already, and it may, at first sight, appear to him a waste of time to go over the same ground again; he should, however, bear in mind that he is now much more competent to understand the explanations of the mysteries of theoretical chemistry, and that only a thorough understanding of the theory of chemistry in general will enable him to become a proficient chemist.

**2. Atomic Theory.**—The atomic theory, on which the science of chemistry is now based, was enunciated at the beginning of the present century, only after the gravimetric and volumetric composition of a large number of compounds had been synthetically, as well as analytically, determined.

The theory arose from the contemplation of the quantitative composition of various compounds, when it was seen that chemical combination does not occur between indefinite quantities of matter, but that its combination is controlled by the three following laws:

1. **Law of Constant Proportions.**—*The proportions, by weight, according to which bodies combine, are invariable for each combination.*

It is this law that determines how much of an element in a mixture will enter into combination. For instance, when a mixture of zinc and sulphur is heated, complete combination will occur only when the ratio of the mass of zinc to that of sulphur is 64.9 : 31.98; if the mixture contains the elements in any other ratio, either zinc or sulphur will remain in an uncombined state after heating.

2. **Law of Multiple Proportions.**—*When two elements combine to form more than one compound, the masses of the one element combining with a constant mass of the other must be simple multiples of the smallest mass among them.*

This law is best illustrated by the case of the oxides of nitrogen given in Art. **35,** *Theoretical Chemistry.* The study of these compounds and that of other similar cases led Dalton, in 1808, to formulate the atomic theory.

3. **Law of Reciprocal Proportions.**—*When an element forms a compound with each of several elements, the masses of the several other elements which combine with a constant mass of the first element are also the masses of these elements which combine with each other, or they bear, at least, some simple ratio to these masses.*

**3.** Thus, for instance, with 32 parts of sulphur there combine 2 parts of hydrogen, 32 parts of oxygen, and 6 parts of carbon, to form separate compounds; accordingly, the mass of oxygen occurring in any compound of this element with carbon must be 32, or twice, three times, one-half, or one-fourth, etc. of 32, for every 6 parts of carbon. Similarly, hydrogen and oxygen must combine in the ratio of 2 : 32 (as

in $H_2O_2$) or of these numbers multiplied or divided by some simple integer, as, for example, in $H_2O$.

In order to account for the existence of these laws, Dalton revived the atomic theory, and laid down the principle that *each of the indivisible particles (atoms), of which a kind of matter is composed, has an invariable weight, and this weight is the same for each atom of the same kind of matter.* And, also, when combination of one kind of matter with another occurs, this union must take place between the atoms of these kinds of matter, and consists in the addition of one or more atoms of the first kind to one or more atoms of the second kind. If these arguments are granted as true, it at once becomes apparent why a compound always contains its elements in the same gravimetric ratio. Water, for instance, is always composed of oxygen and hydrogen in the ratio of 8 : 1 by weight; and this, according to Dalton, is due to the fact that water is a compound of 1 atom of oxygen with 1 atom of hydrogen, the atom of oxygen weighing 8 times as much as the atom of hydrogen; the formula of water should, therefore, be represented by the formula $HO$. The considerations which led to the adoption of $H_2O$ for the formula of water will be dealt with presently.

**4.** The law of multiple proportions follows necessarily from Dalton's hypothesis. For, if a compound of $x$ atoms of one element with $y$ atoms of another element exists, the only way in which a new compound can be formed is by adding another atom or by taking one away; and, since all atoms of the same element have an equal weight, the addition or subtraction of each atom must cause the same variation in the proportional composition. If, for instance, there is a compound of 1 atom of nitrogen with 1 atom of oxygen, and the ratio between the weights of these atoms is 7 : 8, it is evident that another compound can be produced only by adding either one or more atoms of nitrogen, each weighing 7, or one or more atoms of oxygen, each weighing 8; so that any other oxide of nitrogen must contain the elements in the ratio $7 \times n : 8 \times m$ by weight, $n$ and $m$ being integers.

**5.** The third law of chemical combination is just as easily explained; for the ratio by weight in which two elements combine is either the ratio between the weights of their atoms, or that between some multiples of these weights. Consequently, the ratio between the weights of two elements in a compound must be represented by the same numbers as those representing the weights of these elements in their compounds with any third element, or by some simple multiple or submultiple of these weights. If the compound of carbon with sulphur, which contains these elements in the ratio of 12 : 64 parts by weight, contains only 1 atom of sulphur and 1 atom of carbon, then any other compound of sulphur with any other element that is itself capable of combining with carbon in the ratio of $x : 12$ must contain the sulphur in the ratio of $64 : x$, or $64 \times n : x$, $n$ being an integer. If, however, the compound of carbon and sulphur contains 2 or 4 atoms of the latter, other compounds may contain it in the proportion of 32, or 16 parts by weight.

**6.** Dalton constructed a table of atomic weights—that is to say, a table of relative weights—by determining how many parts by weight of each element combine with 1 part by weight of hydrogen, the atomic weight of which he accepted as unity. Since, now, the equivalent of an element is defined as *the number of parts by weight of the element which will combine with or displace 1 part by weight of hydrogen*, it is evident that Dalton's atomic weight was what modern chemistry now calls *chemical equivalents.* This arose from the fact that Dalton did not see the necessity of assuming the existence of a second kind of ultimate particle, as, indeed, is evident from the fact that he refers to the *atoms of compounds*, notwithstanding the paradox evolved in this expression. The necessity of including the molecule in the conception of the structure of matter arose from the discovery of Gay-Lussac in 1808 of the laws controlling the combination of gases by volume. (See Art. **66,** *Theoretical Chemistry.*)

**7.** It will readily be seen that it would be practically impossible to explain the combination of gases without the

hypothesis of the existence of molecules, even if we only choose such an apparently simple combination as that of hydrogen and chlorine as the subject for consideration. Equal volumes of hydrogen and chlorine combine, and the volume occupies twice the volume of either of its constituents—1 volume of $H$ combines with 1 volume of $Cl$ to form 2 volumes of $HCl$. Now, Dalton reasoned that 1 atom of $H$ combines with 1 atom of $Cl$ to form 1 "atom" of $HCl$. If this be true, equal volumes of hydrogen and chlorine must contain the same number of atoms, as it has been proved that equal volumes of these gases combine exactly—i. e., no residue of any of these gases is left. This same reasoning applies to a great number of other gases, wherefrom Gay-Lussac tried to deduce the generalization that equal volumes of gases contain the same number of atoms. But, if this be true, 2 volumes of $HCl$, produced by the combination of 1 volume of $H$ with 1 volume of $Cl$, must contain twice as many atoms as the 1 volume of chlorine or of hydrogen contains; therefore, 1 atom of $Cl$ combines with 1 atom of $H$ to form 2 atoms of $HCl$, and, necessarily, 1 atom of $HCl$ must contain $\frac{1}{2}$ atom of $H$ and $\frac{1}{2}$ atom of $Cl$, which, however, would be contradictory to the theory that an atom is indivisible.

Nevertheless, Gay-Lussac's generalization corrected some of Dalton's atomic weights, and brought us a *step* nearer to our modern theory. Oxygen will serve as a good example of the success of Gay-Lussac's investigation: Two volumes of $H$ combine with 1 volume of $O$ to form water, but equal volumes of gases contain the same number of atoms; therefore, 2 atoms of $H$ combine with 1 atom of $O$. The ratio by weight of $H$ to $O$ in water, however, is 1 : 8, so that 2 atoms of $H$ weighing 1 combine with 1 atom of $O$ weighing 8; but, as already defined, 1 atom of hydrogen is to weigh 1; therefore, water contains 2 atoms of $H$ weighing 2, combined with 1 atom of oxygen weighing 16, and its formula is $H_2O$.

**8.** In the year 1811, Avogadro conceived the existence of two different kinds of particles, *molecules* and *atoms*. Starting with the conception that gases are composed of ultimate

particles which he named *molecules*, he endeavored to explain the combination of gases by volume, but encountered, after all, the same difficulties of a logical explanation that were experienced by Gay-Lussac. To overcome this difficulty, he had recourse to the supposition that the molecules of gases are shattered before combination occurs, and that the parts of the molecules then unite to form the molecules of the new gas. The particles produced by the dissension of the molecules were the true indivisibles, or Dalton's *atoms*. In this manner, Avogadro was enabled to support the generalization now known as *Avogadro's law* (see Art. **24,** *Theoretical Chemistry*).

We will find no difficulty now in explaining the combination of $H$ and $Cl$; that is to say, 1 volume of hydrogen contains the same number of molecules as does an equal volume of chlorine; when these volumes combine, the molecules are shattered, and their component atoms recombine to form the new molecules of hydrogen chloride. One molecule of chlorine thus reacts with 1 molecule of hydrogen to form 2 molecules of hydrogen chloride, which, according to Avogadro's law, must occupy exactly twice the volume of either the hydrogen or chlorine molecule.

**9.** The terms *atom* and *molecule* have been previously defined (see Arts. **3** and **19,** *Theoretical Chemistry*), and the hypothesis that the molecules of most gaseous elements contain 2 atoms may be, if not proved conclusively, at least strongly supported in the following manner: Hydrogen chloride, according to formula, contains half its volume of hydrogen, and therefore half as much hydrogen as is contained in an equal volume of hydrogen; but, as equal volumes of hydrogen and hydrogen chloride contain, according to the before mentioned law of Avogadro, the same number of molecules, it follows that hydrogen chloride contains half as much hydrogen as 1 molecule of hydrogen. Further, 1 molecule of hydrogen chloride is supposed to consist of 1 atom of hydrogen combined with 1 atom of chlorine; therefore, 1 molecule of hydrogen must be assumed to consist of

1 atom of hydrogen with another atom of hydrogen, and the same reasoning must consequently apply to the molecule of chlorine.

**10.** If Avogadro's law is true, it naturally follows that the relative weights of equal volumes of gases must also be the relative weights of the molecules composing those volumes of gases; and, consequently, the molecular weight of an element or compound is determined by the number of times that a volume of it, in the form of a gas or vapor, is heavier than an equal volume of the gas whose molecular weight is to serve as a unit, or standard. This value is known as the *vapor density* of the element or compound in question. As has been previously stated (see Art. **25,** *Theoretical Chemistry*), hydrogen has been adopted as the standard for molecular weight; and, as 1 molecule of hydrogen is assumed to consist of 2 atoms, the molecular weight of this gas is called "2"; so that the molecular weight $M$ of an element or compound is twice its vapor density $D$ (see Art. **26,** *Theoretical Chemistry*), when $H = 1$; or $M = 2\,D$.

**11.** The determination of the vapor density of a substance that is gaseous at the ordinary temperature simply consists in ascertaining the weight of a known volume of the gas, and dividing this weight by that of the same volume of hydrogen at the same temperature and pressure, calculated on the basis of the determined weight of 1 liter of hydrogen (.0896 gram) at 0° and 760 millimeters pressure.

In the process of actual determination, the capacity (say about 500 cubic centimeters) of a globe closed by a stop-cock is determined by weighing the globe, first empty, and then full of water; the weight of the water which it can contain, and, therefore, its volume (1 cubic centimeter of water at 4° weighs 1 gram) is thus obtained.

The dried globe may then be filled with the purified gas, the temperature and pressure being noted at the moment the stop-cock is closed, and again weighed. Let, for instance, the weight of the empty globe be $w$ grams, and that of the globe full of water at 4° be $W$ grams; then the capacity $V$

of the globe in cubic centimeters is $W - w$. Let $W_1$ be the weight of the globe filled with $CO_2$ at 15° and 770 millimeters pressure. Then, $W_1 - w$ grams is the weight of $V$ cubic centimeters at 15° and 770 millimeters pressure. Since the volume of a gas varies inversely as its pressure (see Mariotte's law, Art. **57**, *Physics*, and also, Art. **88**, *Theoretical Chemistry*), and directly as its absolute temperature, i. e., degrees C. + 273 (see Art. **88**, *Theoretical Chemistry*), $V$ cubic centimeters of hydrogen at 15° and 770 millimeters barometer pressure will be

$$V \times \frac{770}{760} \times \frac{273}{288} \text{ cubic centimeters,}$$

at 0° and 760 millimeters pressure, and will weigh

$$V \times \frac{770}{760} \times \frac{273}{288} \times .0000896 = A \text{ grams.}$$

Thus, $\frac{W_1 - w}{A}$ = vapor density of $CO_2$, and $\frac{2(W_1 - w)}{A}$ is the molecular weight of $CO_2$.

When the substance has to be heated to convert it into a gas, the same method may be adopted, the solid or liquid substance being introduced into the globe, which is then heated in a bath of liquid at a sufficiently high temperature to entirely volatilize the substance; the vapor, in escaping from the globe, expels the air, and when no more vapor issues from the narrow orifice of the neck (which in that case would be substituted for the stop-cock) a blowpipe flame is applied to seal this orifice, the temperature of the bath and the pressure of the atmosphere being noted at the moment of sealing. The calculations involved are the same as those stated above. For substances that volatilize at temperatures above that at which glass becomes soft, globes made of porcelain should be employed; these latter, however, can only be sealed by the oxyhydrogen blowpipe. When modified in this way for solids and liquids, the method is known as *Dumas' method.*

**12.** The foregoing method for determining vapor densities consists in weighing a known volume of vapor. The

value can be equally well, and somewhat more easily, ascertained by measuring the volume occupied by a known weight of vapor, an operation which is most easily accomplished by the *Victor Meyer method.* In this, a weighed quantity of the substance is converted into vapor in a vessel containing either air or some other gas, and the volume of air or other gas displaced by the vapor is collected and measured. As an example, the vapor density of alcohol, which boils at 78.3°, was determined by the writer in the following way:

Victor Meyer's apparatus, as shown in Fig. 1, was used. The vaporizing tube *B C*, well closed by a cork *E*, was heated by the vapor of boiling aniline in the tube *A* as long as any bubbles of air passed from the opening of the delivery

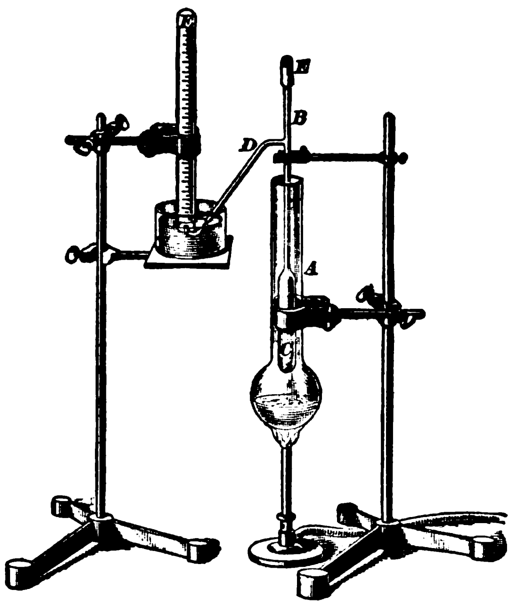


FIG. 1.

tube *D* through the water in the trough. The end of the delivery tube was then inserted into the graduated tube *F* which was full of water. Then .1 gram of alcohol was weighed out into a small tube, made especially for this purpose and closed with a well fitting stopper which could easily

be forced out, and quickly dropped through the opening *E*, into the vaporizing tube *B C*, which was again corked as quickly as possible. A little asbestos had previously been introduced at the bottom of the vaporizing tube in order to avoid its breakage.

At the temperature of the tube the alcohol was at once vaporized. This vapor forced out the stopper of the small containing tube and expelled a volume of air equal to its own volume, which was collected in the tube *F* and accurately measured, with the usual corrections for temperature and pressure. The volume of a known weight of alcohol in the form of vapor having been thus ascertained, its vapor density could be readily calculated. .1 gram of alcohol expelled a volume of air that measured 48.5 cubic centimeters when corrected to 0° and at 760 millimeters pressure; hence, supposing that alcohol could retain the state of vapor at that temperature and pressure, it follows that 48.5 cubic centimeters of alcohol weigh .1 gram. Now, 48.5 cubic centimeters of hydrogen at 0° and 760 millimeters pressure weigh .00434 gram, so that the vapor density of alcohol is $\frac{.1}{.00434} = 23$, and its molecular weight is $23 \times 2 = 46$, the correctness of this test being verified by the established formula of alcohol $C_2H_6O$.

For substances that can be volatilized at extremely high temperatures only, porcelain has to be substituted for glass, and a liquid of high boiling point must be used in the bath surrounding the vaporizing tube.

The student will readily understand that the molecular weight of a compound that is not capable of being vaporized without decomposition cannot be ascertained from its vapor density.

**13. Atomic Weights.**—It has been seen in Art. **8** that there exists a reasonable amount of evidence that the molecules of hydrogen and chlorine, in common with a number of other gaseous elements, contain 2 atoms. If this were universally true, the rule could be established that the atomic weight of an element is half its molecular weight as

determined by its vapor density. This, however, is not always the case, as the student will have already noticed; moreover, many elements cannot be vaporized at sufficiently low temperature to allow a vapor-density determination.

The question now arises, How then are atomic weights obtained? The only reliable and accurate method for determining the atomic weight consists in ascertaining, by quantitative analysis or synthesis, the chemical equivalent of the element, and deciding whether this is identical with the atomic weight or whether it must be multiplied by 2, 3, 4, etc.; this decision is arrived at by one of the three methods hereafter mentioned. The chemical equivalent of an element is the number of parts by weight of it that can combine with either 1 part by weight of hydrogen, 8 parts by weight of oxygen, or 35.5 parts by weight of chlorine; and, as nearly every known element forms at least one known compound with one or the other of these three elements, a determination of the chemical equivalent can usually be accomplished.

The methods commonly employed to determine the relationship existing between the chemical equivalent and the atomic weight of an element are the following:

1. Whereas 2 is accepted as the molecular weight of hydrogen, and since 1 gram of $H$ (at N. T. P.*) occupies 11.16 liters, it follows that the molecular weight of hydrogen expressed in grams is 22.32 liters (at N. T. P.). Since, then, the molecular weight of any other gas is twice the number of times that the gas is heavier than hydrogen, 1 *gram molecule* (i. e., its molecular weight expressed in grams) of every other gas must occupy 22.32 liters. But, as 1 molecule of any compound cannot contain a smaller number of atoms of any of its components than 1—though, of course, it can contain more, its number being practically unlimited—it necessarily follows that 1 gram molecule of any compound cannot contain a smaller quantity than

* The letters N. T. P. are an abbreviated form of "normal temperature and pressure," that is, a temperature of 0° C. and a pressure of 760 mm. of mercury.

1 *gram atom* (i. e., the atomic weight expressed in grams) of any of its elements. Hence, 22.32 liters (at N. T. P.) of any compound gas must contain at least 1 gram atom of each of its constituents, and the atomic weight of an element cannot be larger than the smallest number of grams of the element that can be found in 22.32 liters of any of its gaseous compounds.

On examining, for instance, the multitude of volatile carbon compounds, not one compound, so far at least, has been discovered that contains in 22.32 liters less than 12 grams of carbon; the natural inference is, therefore, that the atomic weight of carbon cannot be more nor less than 12.

This method of determining the atomic weight is widely applicable, since nearly all the elements furnish at least one or two volatile compounds.

2. The second method consists in the application of the relationship of atomic weight to specific heat and the conclusions Dulong and Petit drew therefrom in 1819. This method has been explained at some length in Art. **43**, *Theoretical Chemistry*, and need not be repeated here.

## CHEMISTRY OF THE METALS.

### INTRODUCTION.

**14.** The metals constitute the second and larger part of Inorganic Chemistry. A great number of them are of rare occurrence, others are more abundant, and some are almost universally found diffused through the earth. As a whole, the metals are good conductors of heat and electricity, possess that peculiar luster known as *metallic* luster, and are opaque. Chemically, the metals form oxides which act as bases, while the non-metallic oxides form acids.

**15. Physical Properties of the Metals.**—Though the metals are opaque, or at least usually so described, their opacity is not absolute. A lump of gold, of course, is

opaque, but a thin sheet of gold leaf placed between two plates of glass, allows a passage of a green light through the gold. The same is true of its luster; as a whole, it possesses a fine luster, and a rich yellow color; but it loses this luster when finely divided in the form of powder. When, however, this powder is strongly rubbed with some hard object, as in an agate mortar, or passed under the burnisher, its luster returns. This fact can be noticed in all metals. They lose their metallic luster when finely divided, and regain it by burnishing.

Most of the metals can be crystallized, while some of them are found already crystallized in nature.

Some metals are malleable, others ductile. Mercury is the only liquid metal, while osmium cannot even be melted in the oxyhydrogen flame. Some metals, such as mercury, potassium, zinc, and others, are readily distilled, while others are scarcely volatilized at the highest attainable temperature.

**16. Chemical Properties.**—The metals combine with one another as well as with the metalloids. As a rule, those metals known as the *alkaline* metals, as potassium and sodium, possess the strongest affinities. All metals except platinum combine directly with chlorine, but the chlorides thus formed do not all possess an analogous composition; they contain for one atom of metal a varying number of chlorine atoms. The same is true where oxygen and sulphur, respectively, combine with the metals; from this it follows that the atomic composition of compounds so formed is different.

**17. Alloys.**—The combinations of two metals with each other are called *alloys;* the alloys of mercury are called *amalgams.* As a rule, it is not possible to detect the properties of the individual metals in an alloy; so that an alloy can hardly be considered as a mere mixture ; in many cases, on the other hand, the alteration of properties induced in a metal by the addition of another metal does not show any definite relationship with the mass of the added mass, as would be expected if the alteration were wholly due to chemical combination. It has, hence, become customary to regard alloys

## TABLE 1.

### SOME OF THE MOST IMPORTANT ALLOYS.

| | | |
|---|---|---|
| Gold coin (U. S., France, Germany) | Gold | 900 |
| | Copper | 100 |
| Gold coin (Great Britain) | Gold | 916.6 |
| | Copper | 83.4 |
| Silver coin (U. S.) | Silver | 900 |
| | Copper | 100 |
| Silver coin (Great Britain) | Silver | 925 |
| | Copper | 75 |
| Silverware | Silver | 925 |
| | Copper | 75 |
| Bronze metals | Copper | 93.5–95 |
| | Tin | 6–4 |
| | Zinc | 0.5–1 |
| Gun metal | Copper | 100 |
| | Tin | 10 |
| Bell metal | Copper | 78 |
| | Tin | 22 |
| Speculum metal | Copper | 67 |
| | Tin | 33 |
| Aluminum bronze | Copper | 90–95 |
| | Aluminum | 10–5 |
| Manganese bronze | Copper | 90 |
| | Manganese | 10 |
| Red brass | Copper | 90 |
| | Zinc | 10 |
| White brass | Copper | 65 |
| | Zinc | 35 |
| German silver | Copper | 50 |
| | Zinc | 25 |
| | Nickel | 25 |
| Type metal | Lead | 80 |
| | Antimony | 20 |
| Britannia metal | Tin | 100 |
| | Antimony | 8 |
| | Bismuth | 1 |
| | Copper | 4 |
| Hard pewter | Tin | 92 |
| | Lead | 8 |
| Soft pewter | Tin | 82 |
| | Lead | 18 |
| Plumbers' solder | Tin | 66 |
| | Lead | 33 |

as solidified solutions, and to divide them into two classes; namely, one in which the alloy shows no evidence of chemical combination, and one in which the alloy probably contains a compound of the solvent with the dissolved substance. The majority of alloys belong to the second class, and consist of solutions of compounds of the constituent metals in an excess of one of the metals.

Table 1 gives the composition of some of the more important alloys.

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## METALLIC OXIDES AND HYDRATES.

**18. Formation of Metallic Oxides.**—All metals combine with oxygen, and most of them in several proportions, but the energy displayed by the different metals during combination varies greatly. Many of them become oxidized when simply exposed to the air at more or less elevated temperatures. In this respect it is important to distinguish the action of dry air from that of moist air.

Potassium is the only metal that eagerly absorbs dry oxygen at ordinary temperatures, while all the other metals, except gold, silver, and platinum, only become oxidized at high temperatures. For example, mercury becomes oxidized at 350°, copper when heated to dull redness, and lead readily when in a melted state. This combination frequently produces a luminous heat; iron burns brightly in oxygen, as we have seen from previous experiments, but it becomes necessary to first heat the iron to a bright redness.

A brightly polished sheet of iron will retain its shining surface an indefinite period of time when exposed, at ordinary temperatures, to perfectly dry air; but, if a drop of water falls upon this sheet, or if it is exposed to moist air, rust begins to make its appearance in an incredibly short time. This rust, however, is not an oxide, but ferric hydrate; for the metallic surface of the iron has simultaneously absorbed oxygen and water.

It is generally believed that it is the oxygen of the air dissolved in water that first attacks the metal, and that the

presence of carbon dioxide facilitates the combination. This may be the case or not; the spot of rust, however, once formed, constitutes a voltaic couple with the iron itself, and the current thus established decomposes the water, the oxidation proceeding rapidly through the combination of the oxygen of the decomposed water with the iron.

**19. Composition and Classification of Oxides.**—Not only do the metals differ in the number of atoms of oxygen with which they combine, but they also form several compounds with different numbers of atoms of oxygen; hence, the oxides present not only different compositions, but constitute the different degrees of oxidation, and consequently exhibit different properties.

1. Certain oxides show practically the same constitution as water; namely, 2 atoms of the metal are linked to 1 atom of oxygen. Their formula may be generalized as $M_2O$.

ILLUSTRATION.—

| | |
|---|---|
| Sodium oxide $Na_2O$ | Lithium oxide $Li_2O$ |
| Potassium oxide $K_2O$ | Silver oxide $Ag_2O$ |

2. Other metals can combine with oxygen, atom for atom, and the formula of oxides thus formed may be expressed as $MO$.

ILLUSTRATION.—

| | |
|---|---|
| Barium oxide $BaO$ | Zinc oxide $ZnO$ |
| Strontium oxide $SrO$ | Lead oxide $PbO$ |
| Calcium oxide $CaO$ | Cupric oxide $CuO$ |
| Magnesium oxide $MgO$ | Mercuric oxide $HgO$ |
| Manganous oxide $MnO$ | Stannous oxide $SnO$ |
| Ferrous oxide $FeO$ | |

These oxides, containing but 1 atom of oxygen, are, as a rule, strongly basic; that is, they react energetically with the acids, forming salts.

3. A third variety of oxides, known as *sesquioxides*, contains 2 atoms of a metal linked to 3 atoms of oxygen; their formula may be generalized as $M_2O_3$.

ILLUSTRATION.—

| | |
|---|---|
| Antimony sesquioxide $Sb_2O_3$ | Ferric oxide $Fe_2O_3$ |
| Bismuth sesquioxide $Bi_2O_3$ | Manganic oxide $Mn_2O_3$ |
| Gold sesquioxide $Au_2O_3$ | Chromic oxide $Cr_2O_3$ |
| | Aluminum oxide $Al_2O_3$ |

4. Another variety of oxides contains 1 atom of a metal linked to 2 atoms of oxygen, according to the general formula $MO_2$.

ILLUSTRATION.—

| | |
|---|---|
| Barium dioxide $BaO_2$ | Lead dioxide $PbO_2$ |
| Strontium dioxide $SrO_2$ | ——— |
| Manganese dioxide $MnO_2$ | Stannic oxide $SnO_2$ |

The first four dioxides given as examples are incapable of uniting with acids to form corresponding salts. With hydrochloric acid, they yield, as seen from the subjoined equations, either hydrogen peroxide or chlorine:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

or, should manganese dioxide be heated with sulphuric acid, oxygen would be evolved and manganous sulphate formed:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$

Stannic oxide, on the other hand, is the anhydride of a metallic acid:

$$SnO_2 + H_2O = \underset{\text{stannic acid}}{H_2SnO_3}$$

5. Those oxides that contain 1 atom of a metal linked to 3 atoms of oxygen, and whose formula may be expressed as $MO_3$, possess acid characters still more marked than stannic oxide. An example of this class is chromium trioxide $CrO_3$.

6. Another still more complex class of oxides than the preceding one, and which has obtained the name of *saline oxides*, may be considered as formed by the union of two oxides.

ILLUSTRATION.—

Ferroso-ferric oxide $Fe_3O_4 = FeO + Fe_2O_3$
Manganoso-manganic oxide $Mn_3O_4 = Mn_2O_3 + MnO$
Diplumboso-plumbic oxide $Pb_3O_4 = PbO_2 + 2PbO$

Their formulas may be generalized as $M_3O_4$.

It will be noticed that in the given examples the first two contain 1 molecule of sesquioxide combined with 1 molecule of monoxide, and the last one, 1 molecule of dioxide linked to 2 molecules of monoxide.

**20. General Chemical Properties of the Oxides.**—While some of the metallic oxides are not decomposed by heat, a large number lose either all or part of their oxygen, at more or less elevated temperatures. The oxides of gold, silver, and platinum can be decomposed by heat only. The student will remember, from a previous experiment, that mercuric oxide is decomposed by being heated to redness. Many oxides containing 2 or 3 atoms of oxygen lose only a part of their oxygen atoms, as, for instance, the dioxides of lead and barium.

The simplest oxides, namely, those containing only 1 atom of oxygen, are comparatively the most stable ones; in fact, some of them, when heated in contact with the air, gather oxygen from the air and form higher oxides, as, for instance, is the case when the monoxides of lead, iron, tin, manganese, etc. are heated.

Hydrogen reduces the greater number of the metallic oxides at temperatures more or less elevated, water being formed and the metal liberated. This may be shown by a simple experiment.

EXPERIMENT.—An apparatus similar to the one shown in Fig. 2 is easily fixed up. It consists of a hydrogen-generating flask *A*, to which

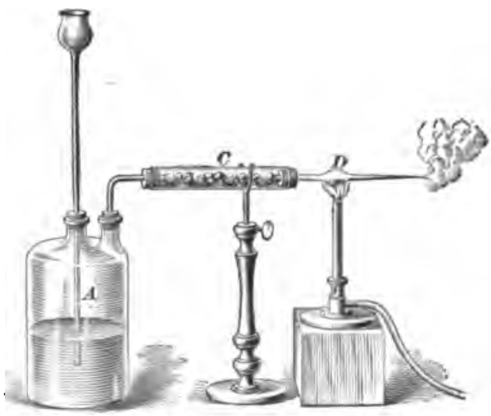


FIG. 2.

is connected, by a perforated cork, a drying tube *C* filled with calcium chloride. To this drying tube is attached a glass tube *D* blown in the

center to a bulb. In this bulb ferric oxide is placed, the generation of hydrogen started, and the bulb heated by means of a Bunsen burner. After some time the ferric oxide will be found to be reduced to a black powder, which is finely divided iron; vapor of water will be seen to escape through the drawn-out point of the bulb.

The reaction that occurred in this experiment may be expressed by an equation thus:

$$Fe_2O_3 + 3H_2 = 3H_2O + 2Fe$$

Instead of ferric oxide, cupric oxide $CuO$ may be used, which when heated in dry hydrogen is reduced to copper, the reaction being so intense that luminous heat is produced.

Carbon reduces the majority of metallic oxides, with the formation of either carbon dioxide or monoxide, as the case may be. Carbon is even more energetic in attacking the metallic oxides, as well as in its actions, than hydrogen; it reduces, for instance, the oxides of potassium and sodium, which have proved irreducible by hydrogen. The oxides of calcium, barium, strontium, magnesium, and aluminum, however, cannot be decomposed by carbon unless exposed to very high temperatures, which can only be obtained by an electrical furnace. The other oxides require for reduction a temperature more or less elevated, according to the affinity the metals possess for oxygen. If the reduction is difficult, a high temperature is required, and carbon monoxide is formed; otherwise, carbon dioxide is one of the products of the reduction.

A small quantity of cupric oxide, for instance, may be reduced by charcoal, if the mixture is heated in a combustion tube by a Bunsen burner, when carbon dioxide is evolved according to the equation:

$$2CuO + C = 2Cu + CO_2$$

On the other hand, to reduce zinc oxide by charcoal, the mixture must be heated to bright redness in a clay retort; in this case, carbon monoxide would be produced according to the equation:

$$ZnO + C = Zn + CO$$

Chlorine, being an extremely active element, readily

decomposes nearly all the oxides at high temperatures, driving out the oxygen and forming, with the remaining metal, a chloride. A few oxides that are irreducible by carbon resist also successfully the attacks of chlorine; such an oxide is aluminum oxide, better known as *alumina.*

If these oxides are, however, simultaneously attacked by carbon and chlorine at high temperatures, they are readily converted into chlorides, with the evolution of carbon monoxide.

Sulphur decomposes all the oxides except alumina and its analogues. The reaction that takes place at high temperatures causes the formation of either a sulphide and sulphurous oxide, or of a sulphide and a sulphate, provided the latter is not decomposable by heat.

If, for instance, cupric oxide is heated with sulphur, the following reaction takes place:

$$4CuO + 3S_2 = 4CuS + 2SO_2$$

but if calcium oxide is heated with sulphur, a sulphide and a sulphate are formed, according to the equation:

$$\underset{\text{calcium oxide}}{4CaO} + \underset{\text{sulphur}}{2S_2} = \underset{\text{calcium sulphide}}{3CaS} + \underset{\text{calcium sulphate}}{CaSO_4}$$

**21. Action of Water on Metallic Oxides.**—If some fragments of sodium or potassium oxide are moistened with water, an energetic reaction immediately takes place. The water unites with the metallic oxides, and they are converted into hydrates; thus,

$$Na_2O + H_2O = 2NaOH$$
$$K_2O + H_2O = 2KOH$$

The sodium hydrate and potassium hydrate thus obtained are soluble in water, and their solutions are caustic, restoring the blue color to reddened litmus paper or to a reddened solution of litmus in water. These hydrates constitute the alkalies.

In the same way, hydrates of barium, strontium, and calcium are formed; these hydrates are not quite as soluble in water, but their solution is still somewhat caustic. Other

hydrates are not soluble in water, but they may be obtained by a double decomposition by precipitating the corresponding salts with an alkali.

If a solution of potassium hydrate is poured into a solution of cupric sulphate, a light-blue precipitate of cupric hydrate is obtained, according to the equation:

$$\underset{\text{cupric sulphate}}{CuSO_4} + \underset{\text{potassium hydrate}}{2KOH} = \underset{\text{potassium sulphate}}{K_2SO_4} + \underset{\text{cupric hydrate}}{Cu(OH)_2}$$

But if this liquid should be heated, even in the liquid from which it was precipitated, it changes its light-blue color into a brown one, being converted into cupric oxide by losing its water; thus,

$$Cu(OH)_2 - H_2O = CuO$$

Quite a considerable number of metallic hydrates undergo the same change on being heated.

There are two metallic acids that contain the elements of an oxide plus the elements of water; these are

$$\underset{\text{chromic acid}}{H_2CrO_4} = \underset{\text{chromium trioxide}}{CrO_3} + H_2O$$

$$\underset{\text{manganic acid}}{H_2MnO_4} = \underset{\text{manganese trioxide}}{MnO_3} + H_2O$$

A consideration of their constitution shows us that they may be compared with sulphuric acid:

$$H_2SO_4 = SO_3 + H_2O$$

but, furthermore, they show an analogy to sulphuric acid in their chemical functions; that is, they, as well as sulphuric acid, contain 2 atoms of hydrogen that may be replaced by a metal.

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## METALLIC SULPHIDES.

**22.** As has been seen in Art. **99**, *Inorganic Chemistry*, Part 1, sulphur is, under certain conditions, an active supporter of combustion, and consequently forms compounds with those metals that burn in its vapor.

The metallic sulphides are analogous in composition to the metallic oxides. The more important of the transformations that the metallic sulphides may undergo are the following:

*Oxygen* has the power of decomposing all sulphides at a more or less elevated temperature. Finely divided potassium sulphide, obtained by calcining the sulphate with an excess of charcoal, is a black powder, which, however, becomes incandescent on contact with oxygen. Its fine state of division naturally favors its ability to absorb oxygen, through the absorption of which it is converted into potassium sulphate; thus,

$$\underset{\substack{\text{potassium}\\\text{sulphide}}}{K_2S} + 2O_2 = \underset{\substack{\text{potassium}\\\text{sulphate}}}{K_2SO_4}$$

*Dry oxygen* acts in exactly the same way on all the sulphides whose corresponding sulphates are stable at high temperatures. If these sulphates are unstable, sulphurous oxide is formed, and a residue of oxide, or sometimes of metal, is obtained if the oxide should be decomposable by heat.

If, for instance, zinc sulphide is roasted, it is converted into zinc oxide, and sulphurous oxide is evolved:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$

but, should sulphide of mercury be heated in a current of air, metallic mercury and sulphurous oxide would result:

$$HgS + O_2 = Hg + SO_2$$

*Moist oxygen* acts, however, still more readily on the sulphides than the dry gas. It unites with them at ordinary temperatures, forming sulphates; thus, for instance,

$$\underset{\substack{\text{sulphide}\\\text{of iron}}}{FeS} + 2O_2 = \underset{\substack{\text{ferrous}\\\text{sulphate}}}{FeSO_4}$$

*Chlorine* attacks all of the sulphides, forming metal chlorides and sulphur chloride, if the dry method be employed, or with the deposition of sulphur, if the reaction takes place in the presence of water.

*Water* dissolves the alkaline sulphides, as well as those of

calcium, barium, and strontium; the sulphides of the other metals are insoluble in water.

*Hydrogen sulphide* combines with certain sulphides, converting them into *sulphohydrates*. The analogy will be noticed between this reaction and that of water on the oxides:

$$K_2S + H_2S = 2KSH$$

| | |
|---|---|
| potassium sulphide | potassium sulphohydrate |

$$K_2O + H_2O = 2KOH$$

| | |
|---|---|
| potassium oxide | potassium hydrate |

## METALLIC CHLORIDES.

**23.** The halogens, *chlorine*, *bromine*, *iodine*, and *fluorine*, form with the metals compounds resembling in appearance and in some of their properties the salts containing oxygen; hence, the compounds of this group with the metals, Berzelius named ***haloid salts***. Thus, he admitted the relationship between these compounds and the oxygen-containing salts, while at the same time he distinguished them by a particular name; for, though they resemble those salts in most of their properties, they differ from them in composition.

**24. Composition.**—All metals except platinum combine directly with chlorine; but they do not all combine in the same atomic proportion, and often the same metal forms several distinct chlorine compounds. They are formed by the union of 1 atom of a metal with 1, 2, 3, 4, or 5, and even 6 atoms of chlorine.

ILLUSTRATION.—

| | | | | | |
|---|---|---|---|---|---|
| $KCl$ potassium chloride | $CaCl_2$ calcium chloride | $SbCl_3$ antimony trichloride | $SnCl_4$ tin tetrachloride | $SbCl_5$ antimony pentachloride | $MoCl_6$ molybdenum hexachloride |
| | $NaCl$ sodium chloride | $FeCl_2$ ferrous chloride | $BiCl_3$ bismuth trichloride | $TiCl_4$ titanium tetrachloride | |
| | $AgCl$ silver chloride | $ZnCl_2$ zinc chloride | $AuCl_3$ gold trichloride | $PtCl_4$ platinum tetrachloride | |

Besides these chlorides, those should be mentioned which are formed by the combination of 2 metallic atoms with 2 or 6 atoms of chlorine:

| | |
|---|---|
| $Cu_2Cl_2$ cuprous chloride | $Al_2Cl_6$ aluminum chloride |
| $Hg_2Cl_2$ mercurous chloride | $Cr_2Cl_6$ chromic chloride |

$Fe_2Cl_6$
ferric chloride

Cuprous chloride $Cu_2Cl_2$ and mercurous chloride $Hg_2Cl_2$ contain, for the same quantity of chlorine, twice as much metal as cupric chloride $CuCl_2$ and mercuric chloride $HgCl_2$. In the first, 2 atoms of copper or mercury are required to unite with 2 atoms of chlorine, and these 2 atoms of metal remain thus associated in all the cuprous and mercurous compounds. It is the same in chloride of aluminum, and in chromic and ferric chloride. Each of them contains 2 atoms of metal intimately associated, and combined, as a whole, with 6 atoms of chlorine.

**25. Properties.**—Most of the chlorides are solid, and possess the color, aspect, and physical properties of the other salts of the same metal. Nearly all are crystalline and soluble in water, with the exception of lead and thallium chloride, which are only slightly soluble, and the chloride of silver, as well as mercurous and cuprous chloride, which are entirely insoluble in water.

The chlorides, as a whole, are very stable compounds, and only those of gold and platinum are entirely decomposed by heat; some of the higher chlorides, however, lose chlorine when calcined, and are thus converted into lower chlorides. Cupric chloride, for instance, is converted into cuprous chloride when heated out of contact with the atmosphere.

Most chlorides are decomposed when heated in a current of hydrogen, hydrochloric acid being evolved and the liberated metal remaining; these decompositions may be ascribed to the very powerful affinity that chlorine possesses for hydrogen.

The action of the metals on the chlorides causes some interesting phenomena which are worth studying.

If mercuric chloride (corrosive sublimate) is mixed with finely powdered tin and heated in a glass retort connected with a receiver, a liquid that diffuses thick vapors in the air will soon be seen to collect in the receiver. On examination, this liquid will be found to be tetrachloride of tin, a substance known to the medieval chemists as *fuming liquor of Libavius.* It is formed by the decomposition of the mercuric chloride, the chlorine combining with the tin, while the metallic mercury is set free.

Bismuth produces the decomposition of mercuric chloride in a similar way.

These experiments may be modified by operating in the presence of water, in which, as has been previously mentioned, most chlorides are soluble; this is the case with mercuric chloride.

If a plate of copper is submerged in a solution of mercuric chloride, the plate immediately becomes coated with metallic mercury. This may be explained by the fact that the mercury of the mercuric chloride is displaced from its combination by the copper, which combines with the chlorine; cupric chloride is formed, and, after the expiration of some time, the liquid will contain only that compound. It acquires a green color, and if we now immerse a zinc plate, the compound is again decomposed, zinc chloride being formed and the copper precipitated.

Thus we see that the metals displace one another from their solutions, according to the energy of their affinities. In this case it is for the possession of chlorine that these metals strive with one another, the metal with the more energetic affinity driving the weaker one out. It must be remarked that in this respect the chlorides behave in the same manner as the oxygen salts.

This analogy is continued in numerous reactions. Solutions of the metallic chlorides enter into double decompositions, like the oxygen-containing salts. If, for instance, potassium hydrate is added to a solution of cupric chloride

and also to a solution of cupric sulphate, it will be found that in each of the solutions a light-blue precipitate of cupric hydrate is obtained. These two analogous reactions may be expressed by the following equations:

$$\underset{\text{cupric chloride}}{CuCl_2} + \underset{\text{potassium hydrate}}{2KOH} = \underset{\text{potassium chloride}}{2KCl} + \underset{\text{cupric hydrate}}{Cu(OH)_2}$$

$$\underset{\text{cupric sulphate}}{CuSO_4} + \underset{\text{potassium hydrate}}{2KOH} = \underset{\text{potassium sulphate}}{K_2SO_4} + \underset{\text{cupric hydrate}}{Cu(OH)_2}$$

There is still another resemblance between cupric chloride and cupric sulphate. When perfectly pure, cupric chloride has a yellowish color; if it is moistened with water, heat is evolved, and it assumes a green color. It has now combined with water, and will easily dissolve, if sufficient water is added. A green liquid is thus obtained, which deposits, by spontaneous evaporation, green prismatic crystals, which are hydrated cupric chloride. They contain water of crystallization, and can only exist on that condition, exactly the same as the crystals of cupric sulphate. Thus, certain metallic chlorides are capable of taking water of crystallization, like the true salts.

This analogy may be completed by one more characteristic:

1. If a solution of aluminum sulphate is added to a concentrated solution of potassium sulphate and the mixture well stirred, an abundant crystalline deposit is obtained, which is a double salt, i. e., *potassium and aluminum sulphate*, better known as *alum*.

2. A yellow precipitate is obtained by adding to a concentrated solution of potassium chloride a solution of platinic chloride. This precipitate is the double chloride of potassium and platinum, and contains all the elements of 2 molecules of potassium chloride and 1 molecule of platinic chloride.

This example proves that the metallic chlorides may combine to form *double chlorides*, in exactly the same manner as the oxygen-containing salts combine to form *double salts*.

The tetrachlorides of tin and titanium are liquids at

ordinary temperatures, while the chlorides of zinc and bismuth, though solids at ordinary temperatures, are fusible at low temperatures.

Most of the chlorides are fusible at high temperatures, and many of them, being volatile, can be distilled without any alteration, as, for instance, the tetrachlorides of tin and titanium and the chlorides of mercury, zinc, bismuth, etc.

## SALTS.

**26.** Salts have been defined, in Art. **57,** *Theoretical Chemistry*, as products formed by the substitution of a metal for the hydrogen of acids. They result from the action of the acids on metallic oxides or hydrates.

It has been seen, in Art. **55,** *Theoretical Chemistry*, that the name *acid* applies to two different kinds, namely, *oxy-acids* and *hydracids;* the student will now be able to understand a more concise definition of these two varieties than that given in Art. **55.**

**Definitions.—Hydracids** *are formed by the union of hydrogen with strongly electronegative elements*, such as chlorine, bromine, etc.; as, for instance, hydrochloric acid $HCl$, hydrobromic acid $HBr$, etc.

**Oxy-acids,** *which are more complicated, contain hydrogen united with a strongly electronegative oxidized group, i. e., a group of atoms formed by oxygen and another element;* as, for instance, sulphuric acid $H_2SO_4$, nitric acid $HNO_3$, etc.

These two classes of acids, though different in composition, behave in the same manner in contact with bases (for the definition of a base, see Art. **56,** *Theoretical Chemistry*).

1. If hydrochloric acid is gradually added to a concentrated solution of potassium hydrate, the liquid becomes heated, and, as it is neutralized by the acid, a white crystalline deposit separates, which increases as the solution cools. This is *potassium chloride.*

2. If diluted sulphuric acid (1 volume of acid to 1 volume of water) is added, drop by drop, to a concentrated solution

of potassium hydrate, the liquid becomes heated, and, as it is neutralized by the acid, a white crystalline deposit separates, which increases as the solution cools. This deposit is *potassium sulphate.*

The student will readily perceive the analogy between the two reactions. In each case the same powerful base, *potassium hydrate,* has been neutralized by an energetic acid, and the reaction has been accompanied in both cases by the evolution of heat, in both cases giving rise to the formation of a saline matter, which has been precipitated. One part of the reaction, however, is invisible; this is the formation of water, which always accompanies the generation of a salt in the ordinary manner, and which is shown in expressing the reactions by equations; thus,

$$(1)\qquad \underset{\text{potassium hydrate}}{KOH} + \underset{\text{hydrochloric acid}}{HCl} = \underset{\text{potassium chloride}}{KCl} + \underset{\text{water}}{H_2O}$$

$$(2)\qquad \underset{\text{potassium hydrate}}{2KOH} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{potassium sulphate}}{K_2SO_4} + \underset{\text{water}}{2H_2O}$$

The student will perceive that these reactions, as expressed by the above equations, consist of an interchange of elements, identical to that explained in Art. **77**, 3, *Theoretical Chemistry*, and which interchange, in fact, is a double decomposition. The hydrogen of the acid is exchanged for the metal of the potassium hydrate, and by the exchange the potassium hydrate is converted into water, while the acid is converted into a salt of potassium. All hydrogen compounds capable of thus exchanging their hydrogen for an equivalent quantity of metal have the functions of acids, and these acids become salts when their hydrogen is thus replaced by a metal. This clearly shows the prominent part hydrogen takes in the formation of salts.

The question now arises, Whence comes this property, this capacity for making such exchanges, and this quality of being replaceable by a metal? Doubtless from the element, or group of elements, with which the hydrogen is united in

the acids; and in this respect chlorine and sulphur play the same parts in hydrochloric and hydrosulphuric acid, respectively, as the oxidized groups play in nitric, sulphuric, and phosphoric acid.

| | | |
|---|---|---|
| $HCl$<br>hydrochloric acid | $H_2S$<br>hydrosulphuric acid | |
| $H(NO_3)$<br>nitric acid | $H_2(SO_3)$<br>sulphurous acid | $H_3(PO_3)$<br>phosphorous acid |
| $H(ClO_3)$<br>chloric acid | $H_2(SO_4)$<br>sulphuric acid | $H_3(PO_4)$<br>phosphoric acid |

This property is most concisely characterized by saying that the elements or groups, to which the hydrogen is united, are strongly electronegative, or acid, in opposition to the hydrogen, which is strongly electropositive, or basic.

When such an acid reacts on an oxide or hydrate, an interchange of elements occurs, and a salt and water are formed; the latter is a constant product necessary to the reaction.

**27. Neutral, Acid, and Basic Salts.**—As salts are formed by the substitution of a metal for the basic hydrogen of an acid, it is evident that their composition must be related to that of the acids from which they are derived. We know that acids contain, as the case may be, 1, 2, or 3 replaceable atoms of hydrogen, i. e., that they are either *monobasic*, *dibasic*, or *tribasic;* and, consequently, the salts must be differently constituted, according as they are derived from monobasic, dibasic, or tribasic acids.

A *neutral*, or *normal*, *salt* may be defined as a salt produced by the entire replacement of hydrogen by an equivalent quantity of metal. This substitution may, however, only be partial; for, when an acid is dibasic, only 1 atom of its hydrogen may be replaced by 1 atom of metal, and there remains in the salt 1 atom of basic hydrogen.

Further, when an acid is tribasic, it may happen that only 1 atom of hydrogen is replaced by 1 atom of metal, and the salt will still retain 2 atoms of basic hydrogen; or, again, 2 atoms of hydrogen may be replaced by an equivalent

quantity of metal, and the salt will retain 1 atom of basic hydrogen.

Whenever basic hydrogen thus remains in a salt, the acid is incompletely saturated, and the salt ordinarily retains the character of an acid—hence its name, *acid salt.*

The following examples clearly illustrate the possible cases of complete and incomplete saturation, which may be presented by a monobasic, dibasic, and tribasic acid:

| | | |
|---|---|---|
| $HNO_3$ | $H_2SO_4$ | $H_3PO_4$ |
| $KNO_3$ | $\left.\begin{matrix}K\\H\end{matrix}\right\} SO_4$ | $\left.\begin{matrix}K\\H_2\end{matrix}\right\} PO_4$ |
| **potassium nitrate** | **potassium acid sulphate** | **monopotassium phosphate** |
| | $K_2SO_4$ | $\left.\begin{matrix}K_2\\H\end{matrix}\right\} PO_4$ |
| | **potassium sulphate** | **dipotassium phosphate** |
| | | $K_3PO_4$ |
| | | **tripotassium phosphate** |

A number of neutral salts are capable of combining with the hydrates or the oxides. The compounds thus formed contain all the elements of the neutral salt, as well as the elements composing the hydrate or oxide, and are known as *basic salts.* The oxides of lead and copper, for instance, may combine with the various salts of lead or copper, and form the basic salts of those metals.

**28.** A given weight of acid requires for its neutralization a fixed and absolutely invariable quantity of a given base; thus, for instance, to convert 1,000 grams of sulphuric acid into a neutral potassium salt, a quantity of 961 grams of potassium oxide $K_2O$ is required. To saturate a given weight of any acid, it is necessary to take such a weight of oxide as will exactly replace all the hydrogen of the acid. While a definite, invariable weight of any particular oxide is required to saturate a given weight of any particular acid, the weights of the different oxides required will vary with their molecular weights.

Thus, 1,000 grams of concentrated sulphuric acid are neutralized by the following quantities of the oxides named.

| | | |
|---|---|---|
| Potassium oxide | 961 | grams |
| Sodium oxide | 632 | " |
| Barium oxide | 1,561 | " |
| Calcium oxide | 571 | " |
| Zinc oxide | 866 | " |
| Cupric oxide | 811 | " |
| Mercuric oxide | 2,204 | " |
| Silver oxide | 2,367 | " |

and again, in order to neutralize 1,000 grams of concentrated nitric acid, the following quantities of the same oxides are required:

| | | |
|---|---|---|
| Potassium oxide | .747 | grams |
| Sodium oxide | 492 | " |
| Barium oxide | 1,214 | " |
| Calcium oxide | 444 | " |
| Zinc oxide | 651 | " |
| Cupric oxide | 631 | " |
| Mercuric oxide | 1,714 | " |
| Silver oxide | 1,841 | " |

The student will notice, on comparing the given weights, that the latter quantities are in the same ratio to each other as are the quantities of oxides to each other, which are necessary to neutralize 1,000 grams of sulphuric acid; namely:

$$961 : 632 :: 747 : 492$$
$$961 : 1,561 :: 747 : 1,214$$
$$961 : 571 :: 747 : 444$$
$$961 : 866 :: 747 : 651$$
$$961 : 811 :: 747 : 631$$
$$961 : 2,204 :: 747 : 1,714$$
$$961 : 2,367 :: 747 : 1,841$$

A German chemist, Richter, of Berlin, living at the end of the last century, was the first to notice this fact, and from

his observations established the law concerning the composition of salts. *The quantities of oxides that neutralize a given weight of one acid are proportional to the quantities of the same oxides that neutralize the same weight of another acid.*

Richter also investigated the phenomenon of the precipitation of metallic solutions by metals. It is a well known fact that, when a piece of iron is plunged into a solution of cupric sulphate, the iron dissolves, displacing a certain quantity of copper, without any other change. Since the new salt formed (ferrous sulphate) exists in the solution in the same condition of neutrality as the cupric sulphate, *the quantities of metal that thus displace each other must be equivalent.* As neither oxygen nor acid is liberated, it is evident that the respective quantities of each metal in the salt successively formed must be united to the same quantity of oxygen. It has even been suggested that, in the salts containing, like the sulphates, 4 atoms of oxygen, the metal is only closely connected to 1 atom of oxygen, which, by itself, would be entirely sufficient to constitute the metal in the state of a monoxide:

$$CuSO_4 = CuOSO_3$$

$$FeSO_4 = FeOSO_3$$

If this were the case, it is evident that, when cupric sulphate is decomposed by iron, the quantity of metal that enters into solution would combine with precisely the quantity of oxygen abandoned by the copper. This quantity of oxygen being constant, the quantitiès of metals that combine successively with it, naturally must differ, while being equivalent to one another; and it is evident that the oxides thus formed would be richer in oxygen, as the weight of metal entering into solution is less considerable. Or, in other words, *the richness of these oxides in oxygen is inversely proportional to the weights of the metals that successively become dissolved;* and it was in this form that Richter formulated the second law of the composition of salts.

**29. Properties of Salts.**—The salts occur in various colors; those formed by an acid possessing a color adopt the color of the acid, as is the case with manganates, permanganates, and chromates.

Most of the colored oxides form salts showing various colors.

ILLUSTRATION.—

Ferrous salts are bluish green.
Ferric salts are yellow to yellowish brown.
Manganese salts are pink.
Chromium salts are either dark green or red.
Nickel salts are green.
Cobalt salts are currant red or blue.
Cupric salts are blue or green.
Gold salts are yellow.

These various colors, however, are, as a rule, only developed when the salts are hydrated; i. e., combined with water of crystallization. It has been further found that the less soluble a salt is, the less taste it exhibits, and that this taste is only more or less pronounced in the soluble salts. The taste naturally varies widely; while the salts of magnesium are bitter, those of iron are astringent with a decided metallic after taste, the salts of lead are, at the same time, sweet and astringent, and the salts of copper, antimony, and mercury have an acrid metallic taste that is decidedly nauseating.

The salts occur, as a rule, in crystalline form, though some of them may be obtained as amorphous precipitates; but even these salts, when formed slowly and under conditions favoring crystallization, may be obtained in some crystalline form.

**30. Action of Water on the Salts.**—If water is poured upon powdered chalk in a glass vessel and the mixture stirred, a white, cloudy liquid is obtained; and, if the liquid is allowed to stand undisturbed for a time, it will be seen that the water becomes clear again and that the chalk has settled upon the bottom of the vessel. From these facts it is evident that the chalk could not have been dissolved by the water, but was simply suspended in it.

If, on the other hand, we take some potassium nitrate

(generally known as *saltpeter*) and add it to clean water, we soon notice that the saltpeter has disappeared, and also that the water has not changed its appearance. The saltpeter is melted by the water, as we commonly express it; that is, the saltpeter is dissolved by the water and is thus uniformly diffused through it. It has itself become a liquid; this is the phenomenon of *solution*. If we are more exact in our work and place a thermometer in the water before adding the saltpeter, a reduction of the temperature of the water will be noticed as the saltpeter dissolves; this may be explained by the fact that the saltpeter must absorb heat in assuming the liquid state and becoming diffused throughout the water.

If we continue to add saltpeter, the solid disappears for some time, till after a little while the water ceases to dissolve it any longer, or, as it is generally expressed, till the solvent power of the water is exhausted. The water is then said to be *saturated* with the salt, and any excess of saltpeter added will remain in the solid state.

If we now begin to heat the solution, this excess in its turn is readily dissolved, for the solubility increases with the temperature; and, as the latter is elevated, a larger quantity of salt is dissolved. This continues until the water reaches its boiling point, when its solubility reaches its limit.

If, now, this boiling saturated solution is allowed to cool, it deposits a large portion of the salt in crystalline form; in this manner, voluminous, colorless, and transparent prisms are obtained which fill the vessel, and are surrounded by a solution of saltpeter, saturated at the temperature to which the liquid has been cooled; this liquid is called the *mother liquor* of the crystals. It is in this manner that soluble salts are crystallized by cooling their hot saturated solutions.

These same facts are observed for other soluble salts; generally speaking, their solubility increases with the temperature. There are, however, certain exceptions; sodium chloride is only slightly more soluble in hot than in cold water, and calcium sulphate is much more soluble in cool than in boiling water.

We have just seen that a saturated solution of a salt at a

given temperature generally deposits part of its salt on cooling; there are, however, again exceptions. It sometimes happens, if the cooling takes place under certain conditions, that a portion of the salt, which, through the difference in the temperature, should be reduced to the solid state, remains in solution; the solution is then said to be *supersaturated.* Sodium sulphate and alum possess a great tendency to form such supersaturated solutions.

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### METALLIC NITRATES.

**31.** Nitric acid has the composition $HNO_3$; therefore, the nitrates contain the group $NO_3$ linked to a metal which has replaced the hydrogen atom of the acid. They contain one or more groups of $NO_3$, according to the valence of the metal, which has neutralized the nitric acid; as, for instance,

$$\underset{\text{potassium hydrate}}{K'OH} + \underset{\text{nitric acid}}{HNO_3} = \underset{\text{potassium nitrate}}{K'NO_3} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{plumbic oxide}}{Pb''O} + \underset{\text{nitric acid}}{2HNO_3} = \underset{\text{plumbic nitrate}}{Pb''(NO_3)_2} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{bismuth hydrate}}{Bi'''(OH)_3} + \underset{\text{nitric acid}}{3HNO_3} = \underset{\text{bismuth nitrate}}{Bi'''(NO_3)_3} + \underset{\text{water}}{3H_2O}$$

**32.** All metallic nitrates are soluble in water; some of them are deposited from their solutions in the form of hydrated crystals, as, for instance, *cupric nitrate*, which crystallizes with 6 molecules of water at low temperatures; other nitrates are deposited in anhydrous crystals, as, for example, the nitrates of *sodium*, *potassium*, *barium*, and *silver*.

All metallic nitrates are decomposed by heat, the products of decomposition depending on the nature of the nitrate and the temperature to which they are subjected. Potassium nitrate, for instance, is first transformed into nitrite, which is finally decomposed into nitrogen, oxygen, and potassium

oxide. Silver nitrate yields nitrogen tetroxide (nitryl), oxygen, and a residue of silver, according to the equation:

$$2AgNO_3 = N_2O_4 + O_2 + Ag_2$$

All nitrates liberate oxygen under the influence of heat, and they are easily reduced by bodies possessing a strong affinity for oxygen. Sulphur, charcoal, and a number of metals are strongly oxidized when heated with the nitrates.

If sulphur is heated with potassium nitrate, potassium sulphate is formed, and sulphurous oxide and nitrogen are set free:

$$\underset{\substack{\text{potassium}\\\text{nitrate}}}{2KNO_3} + \underset{\text{sulphur}}{S_2} = \underset{\substack{\text{potassium}\\\text{sulphate}}}{K_2SO_4} + \underset{\substack{\text{sulphurous}\\\text{oxide}}}{SO_2} + \underset{\text{nitrogen}}{N_2}$$

When powdered potassium nitrate is thrown upon burning charcoal, the salt melts and helps to increase the combustion of the charcoal, thus producing a vivid deflagration, potassium carbonate being formed and carbon dioxide and nitrogen disengaged, according to the subjoined equation:

$$\underset{\substack{\text{potassium}\\\text{nitrate}}}{4KNO_3} + \underset{\text{carbon}}{5C} = \underset{\substack{\text{potassium}\\\text{carbonate}}}{2K_2CO_3} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{3CO_2} + \underset{\text{nitrogen}}{2N_2}$$

**33.** Some of the characteristic properties of the metallic nitrates are (1) they deflagrate when thrown upon incandescent charcoal; (2) when brought in contact with concentrated sulphuric acid they evolve white vapors of nitric acid; (3) when mixed with copper filings and then treated with concentrated sulphuric acid, red vapors are evolved.

When the solution of a nitrate is mixed with its own volume of concentrated sulphuric acid, and a crystal of ferrous sulphate is introduced into the liquid, the crystal very soon assumes a brown color, which is communicated to the liquid. In this very delicate reaction, the nitric acid is reduced by the ferrous sulphate to nitrogen dioxide, which colors the excess of ferrous sulphate brown.

The solution of a nitrate when treated with sulphuric acid will decolorize a solution of sulphate of indigo when the liquid is heated to boiling.

## METALLIC SULPHATES.

**34. Composition.**—Sulphuric acid $H_2SO_4$, being dibasic, contains 2 atoms of replaceable hydrogen; when both of these atoms are replaced by an equivalent metal, a neutral sulphate is formed, while an acid sulphate results when only 1 atom of the 2 is replaced. The hydrogen atoms of this are also removed by the oxygen of the metallic oxide or hydrate that more or less completely saturates the sulphuric acid, as shown by the subjoined four different equations:

(1) $\underset{\text{potassium hydrate}}{K'OH} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{potassium acid sulphate}}{K'HSO_4} + \underset{\text{water}}{H_2O}$

(2) $\underset{\text{potassium hydrate}}{2K'OH} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{potassium sulphate}}{K_2'SO_4} + \underset{\text{water}}{2H_2O}$

(3) $\underset{\text{plumbic oxide}}{Pb''O} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{plumbic sulphate}}{Pb''SO_4} + \underset{\text{water}}{H_2O}$

(4) $\underset{\text{aluminum oxide}}{Al_2^{vi}O_3} + \underset{\text{sulphuric acid}}{3H_2SO_4} = \underset{\text{aluminum sulphate}}{Al_2^{vi}(SO_4)_3} + \underset{\text{water}}{3H_2O}$

These examples bear evidence that all the sulphates contain the group $SO_4$, which is in sulphuric acid linked to 2 atoms of hydrogen; and, since this group is divalent, it becomes necessary that it shall be linked to an atom or atoms of a metal equivalent to 2 atoms of hydrogen.

1. In the acid sulphates the group $SO_4$ is united with an atom of hydrogen and an atom of a monovalent metal; the formula may be generalized thus, $R'HSO_4$.

2. In neutral or normal sulphates the group $SO_4$ is linked to 2 atoms of a monovalent metal according to the formula $R_2'SO_4$.

3. The group $SO_4$ is linked to 1 atom of a divalent metal according to the formula $R''SO_4$.

4. These cases seem very plain and simple. The fourth case is just as plain and simple, although at first glance it does not appear to be. Here we have to consider the

saturation of $H_2SO_4$ by an oxide $R_2O_3$. Each of the 3 atoms of oxygen of the oxide represented by $R_2O_3$ removes $H_2$ from a molecule of $H_2SO_4$, and the result is that the metal that was linked to $3O''$ combines with $3(SO_4)''$. The 2 atoms of metal substituted for $3H_2$ in 3 molecules of $H_2SO_4$ are then equivalent to 6 atoms of $H$. They are hexavalent, as is indicated by the Roman numeral VI.

**35. General Properties of the Metallic Sulphates.** The sulphates of barium, strontium, and lead are almost absolutely insoluble in water, and mercurous, calcium, and silver sulphates are only slightly soluble in it, but all other sulphates dissolve very readily in this medium.

All sulphates, except those of calcium, barium, strontium, magnesium, lead, and the alkaline sulphates, are decomposed by heat at more or less high temperatures. A residue of oxide generally remains when sulphurous oxide and oxygen are liberated. The decomposition of copper sulphate, for instance, may be expressed by the following equation:

$$\underset{\text{cupric sulphate}}{2CuSO_4} = \underset{\text{sulphurous oxide}}{2SO_2} + \underset{\text{oxygen}}{O_2} + \underset{\text{cupric oxide}}{2CuO}$$

Should the oxide be reducible by heat, the residue would naturally consist of the metal solely; as, for instance,

$$\underset{\text{mercuric sulphate}}{HgSO_4} = \underset{\text{mercury}}{Hg} + \underset{\text{sulphurous oxide}}{SO_2} + \underset{\text{oxygen}}{O_2}$$

Those sulphates that may be represented by the general formula $R_2^{vi}(SO_4)_3$ are, as a rule, decomposed at a comparatively low temperature, disengaging vapor of sulphuric oxide and leaving a residue of metallic sesquioxide; thus,

$$\underset{\text{ferric sulphate}}{Fe_2(SO_4)_3} = \underset{\text{ferric oxide}}{Fe_2O_3} + \underset{\text{sulphuric oxide}}{3SO_3}$$

The metallic sulphates are readily reduced by bodies possessing a strong affinity for oxygen, such as charcoal, for instance.

If a mixture of potassium sulphate and an excess of finely

powdered charcoal are heated to bright redness, and then allowed to cool out of contact with the air, a black powder is obtained, which produces a shower of sparks when thrown up into the air. Gay-Lussac calls this mixture *pyrophorus;* it owes its spontaneous inflammability on contact with the air to the finely divided potassium sulphide that it contains, which attracts oxygen with great eagerness. The sulphide is formed according to the following reaction:

$$\underset{\text{potassium sulphate}}{K_2SO_4} + \underset{\text{carbon}}{4C} = \underset{\text{carbon monoxide}}{4CO} + \underset{\text{potassium sulphide}}{K_2S}$$

In the same manner, barium sulphate and calcium sulphate are converted into sulphides by the action of charcoal at a high temperature.

Other sulphates are similarly reduced under the same circumstances, but their products vary; carbon dioxide or carbon monoxide and sulphurous oxide are disengaged, and the residue consists of either metallic oxide or metal.

**36.** Some of the characteristic features of the metallic sulphates are that when treated with sulphuric acid they do not evolve any gas, and when thrown upon burning charcoal they do not deflagrate. Their solutions give a white precipitate of barium sulphate with barium nitrate, which is insoluble in nitric acid. When this precipitate is washed, dried, and calcined with an excess of charcoal, it leaves a residue of barium sulphide; and, when this is moistened with hydrochloric acid, it evolves hydrogen sulphide, which may be easily recognized by its characteristic odor.

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## METALLIC CARBONATES.

**37.** Carbonic acid is assumed to be dibasic like sulphuric acid, and, as it is not known to exist in the state of hydrate, the metallic carbonates are formed by the direct union of carbon dioxide with the metallic oxides or hydrates.

Freshly burned lime $CaO$, on being exposed to the air,

absorbs moisture from it, and also attracts any carbon dioxide that the air may contain, the result being that the lime is converted into calcium carbonate:

$$CO_2 + CaO = CaCO_3$$

It is evident, then, from this equation that the metallic carbonates contain the group $CO_3$, which is linked to a metal; in carbonic acid this group would be linked to 2 atoms of hydrogen, and the composition of the more simple carbonates may be expressed by the subjoined formulas:

$H_2CO_3$, carbonic acid (known only in aqueous solution),

$R'HCO_3$, acid carbonates (bicarbonates),

$\left.\begin{array}{l} R_2'CO_3 \\ R''CO_3 \end{array}\right\}$ neutral carbonates.

**38. Properties.**—With the exception of the alkaline carbonates, all the others, though soluble in water charged with carbonic acid, are entirely insoluble in pure water.

The soluble carbonates, as well as the acid carbonates of the alkaline metals, which are generally known as *bicarbonates*, and of which potassium bicarbonate $KHCO_3$ is an example, possess an alkaline reaction.

All the carbonates except the alkaline carbonates are decomposable by heat, carbon dioxide being disengaged, leaving a residue of metallic oxide, or, if the oxide is decomposable by heat, a residue of metal. Thus, the carbonates of magnesium, calcium, zinc, lead, and copper leave a residue of oxide, while silver carbonate leaves a residue of metal.

All bodies possessing a strong affinity for oxygen act on the carbonates as on the oxides; the metal is reduced if the base is reducible. Charcoal acts in this manner on the carbonates.

If cupric carbonate is heated with charcoal, carbon dioxide is disengaged and the residue is metallic copper; thus,

$$\underset{\text{cupric carbonate}}{2CuCO_3} + \underset{\text{carbon}}{C} = \underset{\text{carbon dioxide}}{3CO_2} + \underset{\text{copper}}{2Cu}$$

In this experiment carbon dioxide is disengaged, as cupric oxide is easily reducible by charcoal. The same, however, cannot be said of potassium oxide; hence, potassium carbonate is only reduced by charcoal at very high temperatures, with the liberation of carbon monoxide, as is shown by the following equation:

$$\underset{\text{potassium carbonate}}{K_2CO_3} + \underset{\text{carbon}}{2C} = \underset{\text{carbon monoxide}}{3CO} + \underset{\text{potassium}}{K_2}$$

or, when barium carbonate is heated with charcoal, carbon monoxide is liberated; but, as barium oxide is not reducible by charcoal, the residue is the metallic oxide and not the metal, as shown in the subjoined equation:

$$\underset{\text{barium carbonate}}{BaCO_3} + \underset{\text{carbon}}{C} = \underset{\text{carbon monoxide}}{2CO} + \underset{\text{barium oxide}}{BaO}$$

Phosphorus readily decomposes all carbonates. If, for instance, a small piece of phosphorus is placed at the bottom of a test tube, the latter then nearly filled with well dried sodium carbonate, and that part of the tube containing the carbonate heated over the Bunsen burner to redness, the phosphorus will thus indirectly become heated, and its vapor will pass through the incandescent carbonate, decomposing it, with the formation of sodium phosphate and a deposition of carbon. After cooling, the contents of the tube will have acquired a black color.

All carbonates when treated with sulphuric acid evolve a colorless, incombustible gas (carbon dioxide), which extinguishes burning bodies and produces a milkiness when conducted into lime water.

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## CLASSIFICATION OF ELEMENTS.

**39. The Periodic Law.**—It has been already shown that the elements may be classified into groups (the student will remember the so called "halogen group of elements") which contain individuals possessed of similar chemical properties.

In the year 1864, Newlands showed that, when the elements are arranged in the order of their atomic weights, this similarity is seen to exist between every eighth element, the first being similar to the eighth, the second to the ninth, and so on. Mendeléef and Lothar Meyer made a similar discovery in 1869.

In seeking for a basis for a true classification of the elements, it is natural that the chemist should turn to the most strictly chemical property of the elements, that is, their tendency to combine with one another. Mendeléef, through his investigations in this direction, proved that the limit of this tendency may be expressed by saying that one equivalent of an element never combines with more than eight equivalents of another element. If, for instance, oxygen and hydrogen are taken as typical elements, it will be noticed that there are never more than 4 atoms of oxygen or 4 atoms of hydrogen united to 1 atom of an element. Furthermore, the sum of the equivalents of $O$ and $H$ that can combine with 1 atom of an element is 8. Thus, if an element "$R$" forms as its highest salt-forming oxide (capable of behaving as an anhydride or as a base) a compound of the type $RO_2$, it will form a hydride $RH_4$; if an oxide $RO_3$, a hydride $RH_2$, and so on. For instance, $N$ forms $N_2O_5$ as its highest oxide—that is, a compound of 5 equivalents of oxygen with 1 atom of nitrogen—and its highest anhydride is $NH_3$; $S$ forms $SO_3$ (6 equivalents of $O$), and its maximum anhydride is $SH_2$. Chlorine forms $ClH$; so that its highest salt-forming oxide should be $Cl_2O_7$ (7 equivalents of $O$ to 1 atom of $Cl$), which, however, is only known in such compounds as

$$K_2OCl_2O_7 = 2KClO_4.$$

It follows that there are 8 types of higher salt-forming oxides which may be presented, thus:

$$R_2O,\ R_2O_2,\ R_2O_3,\ R_2O_4,\ R_2O_5,\ R_2O_6,\ R_2O_7,\ R_2O_8$$

Those elements that form higher salt-forming oxides of the same type are alone analogous. If this proposition be admitted, the elements must be classified in 8 groups. Such a classification reveals the fact that, when the elements are

arranged in order of their atomic weights, they follow the same order as that of their higher oxides, so that the *valence* of the elements towards oxygen returns to the same value at every eighth element, that is, *periodically*. This return is noticeable in the case of all other properties of the elements that have been so far accurately examined; hence the law: *The properties of the elements are periodic functions of their atomic weights.* Or, in other words, *if the elements are arranged in the order of their atomic weights, the properties of consecutive elements will be found to differ, but the properties will return to approximately the same value at definite periods.*

Such an arrangement of the elements is shown in Table 2.

**TABLE 2.**

| Groups. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. |
|---|---|---|---|---|---|---|---|---|
| Series 1 | . *H* | — | — | — | — | — | — | — |
| Series 2 | *Li* . | *Be* . | *B* . | *C* . | *N* . | *O* . | *F* . | |
| Series 3 | . *Na* | . *Mg* | . *Al* | . *Si* | . *P* | . *S* | . *Cl* | |
| Series 4 | *K* . | *Ca* . | *Sc* . | *Ti* . | *V* . | *Cr* . | *Mn* . | *Fe*: *Co*, *Ni*, *Cu* |
| Series 5 | .(*Cu*) | . *Zn* | . *Ga* | . *Ge* | . *As* | . *Se* | . *Br* | |
| Series 6 | *Rb* . | *Sr* . | *Y* . | *Zr* . | *Nb* . | *Mo* . | — . | *Ru*:*Rh*, *Pd*, *Ag* |
| Series 7 | .(*Ag*) | . *Cd* | . *In* | . *Sn* | . *Sb* | . *Te* | . *I* | |
| Series 8 | *Cs* . | *Ba* . | *La* . | *Ce* . | *Di* . | — . | — . | — — — — |
| Series 9 | . — | . — | . — | . — | . — | . — | . — | |
| Series 10 | — . | — . | *Yb* . | — . | *Ta* — | *W* — | — . | *Os*: *Ir*, *Pt*, *Au* |
| Series 11 | .(*Au*) | . *Hg* | . *Tl* | . *Pb* | . *Bi* | . — | . — | |
| Series 12 | — . | — . | — . | *Th* . | — . | *V* . | — . | |
| Higher oxide type | $R_2O$ | $R_2O_2$ ($RO$) | $R_2O_3$ | $R_2O_4$ ($RO_2$) | $R_2O_5$ | $R_2O_6$ | $R_2O_7$ | $R_2O_8$ ($RO_4$) |
| Hydrides | | | | $RH_4$ | $RH_3$ | $RH_2$ | $RH$ | |

**40.** In compiling this table, two difficulties arose. In the first place *Co*, being next to *Fe* in atomic weight, should have been placed in Group I, but neither this metal nor *Ni* shows any analogy with Group I. *Cu*, on the other hand,

shows some analogy with the elements of both Group VIII and Group I, hence its true position appears somewhat doubtful. Thus, *Co* and *Ni* have to remain in Group VIII, an arrangement also necessary in the case of *Rh*, *Pd*, *Ir*, and *Pt*.

In the second place, the element *Ru*, which is next in atomic weight to *Mo*, should come in Group VII, but its position there is untenable, because its higher oxide is of the type $RO_4$ and not $R_2O_7$. Consequently, *Ru* must be placed in Group VIII, while the position in Group VII remains vacant, for the present at least. Again, the average difference between the atomic weights of consecutive elements in the horizontal rows is approximately 2.5, but the difference between the atomic weight of *Ce* and of *Yb* is about 31.5, thus leaving vacant about 13 positions on the table; these are increased to at least 15 by the fact that *Yb* undoubtedly forms a higher oxide $Yb_2O_3$, and cannot, therefore, occur in Group II. Thus, the whole of the ninth row remains, at present, vacant. It may be said at once that where such blanks occur elements are believed to exist, but are as yet unknown. Credence is afforded to this view by the fact that the number of such blanks was larger when the table was first drawn up, some of these spaces having been since filled by the discovery of elements (such as *Ga*, *Ge*, and *Sc*), the atomic weights of which showed that they were the missing elements.

**41.** It will be found that elements in the same group and in even series are completely similar to each other, as, for instance, *Ca*, *Sr*, and *Ba*; this is also the case with the elements in the same group and in odd series, such as *P*, *As*, and *Sb*. The members of odd series, however, do not so closely resemble those of the even series, though in the same group. Thus, *Ca* and *Zn* have fewer properties in common than have *Ca* and *Sr*. It seems, then, that the periodic return of properties to the same value only occurs after two series have been traversed, so that each *period* of the table is constituted by two series; thus, *K*, *Rb*, and *Cs* resemble each other very closely. It will be seen that, since this is the case, each group must consist of two subgroups, indicated in

the table by the setting of the symbols in two vertical lines in each group.

The members of these subgroups, or *families*, resemble each other more closely than do the members of a group taken as a whole. While this is true of the elements that follow *Na*, it is not true up to this point; thus, *Be* is more nearly allied to *Mg* than to *Ca*; *B* to *Al* than to *Sc*; and *C* to *Si* than to *Ti*. These elements, consequently, do not appear to be in their right places, a difficulty that is, however, met by supposing that these elements and those from *Na* to *Cl* (inclusive) constitute two short periods; these elements have been termed the *typical elements* of the table.

**42.** It is only possible here to call attention to a very few of the properties of the elements that return periodically to about the same value. The elements of the same family form oxides that, when bases, are of the same order of basicity, and, when acid oxides, are of the same order of acidity; this is well illustrated by *K*, *Rb*, *Cs*; *Sr*, *Ba*; *P*, *As*, *Sb*.

The specific gravities of the elements exhibit a periodicity; instead, however, of comparing specific gravities, it is better to compare *atomic volumes* (i. e., the number of unit volumes in the atomic weight). The atomic volume of an element is the quotient of its atomic weight divided by its specific gravity at the melting point. Those elements that are most chemically active have the lowest specific gravities, and, therefore, the highest atomic volumes; thus, it is found that the atomic volume falls from the beginning to the middle of a series, but rises again from the middle to the end; for instance, the atomic volume of *K* is 45, of *Ni* 6.8, and of *Br* 26. In the same family, the atomic volume rises with the atomic weight; for instance, $Li = 12$, $K = 45$, $Rb = 57$, $Cs = 71$. Similar relations are maintained between the *molecular volume* (molecular weight divided by specific gravity) of the oxides and some other compounds of the elements.

The melting points of the elements in the same family decrease with the rise of atomic weight; thus, *Li* melts at 180°, *K* at 85°, *Rb* at 39°, and *Cs* at 27°.

**43.** The strongest evidence of the truth of a law of nature is its power to predict. In the periodicity table, certain gaps will be noticed to which no known element belongs. Mendeléef undertook to predict the properties of some of these undiscovered elements, basing his prediction on the periodic law. He pointed out that, in general, the value of any property of an element is the mean of the values of the same property of the elements on the two sides of it, whether in the same group or in the same series with it. Thus, for instance, taking the atomic weights, the densities, and the atomic volumes for selenium, we find:

| Atomic Weights. | | | Densities. | | | Atomic Volumes. | | |
|---|---|---|---|---|---|---|---|---|
| | *S* 31.98 | | | *S* 2.04 | | | *S* 15.7 | |
| *As* 74.9 | *Se* 78.87 | *Br* 79.76 | *As* 5.67 | *Se* 4.6 | *Br* 2.97 | *As* 13.2 | *Se* 17.2 | *Br* 26.9 |
| | *Te* 126.3 | | | *Te* 6.25 | | | *Te* 20.2 | |

To four elements thus related, Mendeléef has given the name *atomic analogues*. At the time of preparing his first table, gaps existed in it between boron and yttrium, between aluminum and indium, and between silicon and tin; to these gaps he assigned elements having the provisional names *ekaboron*, *ekaluminum*, and *ekasilicon*, respectively, and the properties of which he minutely predicted. In 1875, Lecoq de Boisbaudran discovered *gallium*, which proved to have identically the properties predicted for ekaluminum. In 1879, Nilson discovered *scandium*, whose properties turned out to be exactly those required by ekaboron; and in 1886, Winkler discovered *germanium*, an element having properties identical with those which Mendeléef had assigned to ekasilicon.

There would seem to be but little question, therefore, considering this power of prediction, that the periodic law is one of the most fundamental of all the laws of chemical science.

**44.** The periodicity table, however, has found a twofold application, as, besides predicting the properties, etc. of

undiscovered elements, it has afforded a means for deciding the atomic weights of some elements.

This second application of the table is illustrated (1) by the fixation of the atomic weight of beryllium, and (2) by the correction of the atomic weight of tellurium. The equivalent of beryllium is 4.5 and its atomic weight was at first assumed to be 13.5, because its oxide was supposed to be $Be_2O_3$ on account of its similarity to $Al_2O_3$. With this atomic weight, however, that element would have to follow carbon in the periodicity table, a position certainly at variance with its properties. It was therefore suggested that its atomic weight was really 9, in which case its oxide would be $BeO$, and the element would fall into the then vacant place in Group II, a position that has since been confirmed by the determination of the vapor density of $BeCl_2$, from which the maximum atomic weight of 9 is obtained.

The atomic weight of tellurium was formerly given as 128, and in Table 6, *Theoretical Chemistry*, it is given as 126.52. The atomic weight 128 would place tellurium after iodine in the periodicity table, and the weight 126.52 would probably do the same; thus, throwing iodine into Group VII, a position it is incompetent to hold. Recent investigations have indicated that the samples used in making these determinations probably contained other elements, and that the values are too high. Probably the true atomic weight is nearer 125.

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## POTASSIUM.

*Symbol K. Atomic weight 39.04. Valence I.*

**45. History and Occurrence.**—The discovery of potassium dates back to 1807, when Sir Humphry Davy, by submitting potassium hydrate to electrolysis, obtained this metal; soon after, Gay-Lussac and Thenard prepared it chemically in the pure state.

Though rather abundant in nature, it is only found in combinations, and never pure. In the mineral kingdom, potassium occurs as nitrate or niter, as chloride or sylvite, as

potassio-magnesium chloride or carnallite, and as sulphate or aphthitalite. It is also found in various combinations in the waters of the ocean and mineral springs, as well as in land plants, and it appears to be essential to animal life.

**46. Preparation and Properties.**—Little was known of the composition of potassium hydrate until Sir Humphry Davy decomposed it and thus obtained metallic potassium. At present it is prepared by decomposing potassium carbonate by carbon at high temperature, according to the equation:

$$\underset{\substack{\text{potassium}\\\text{carbonate}}}{K_2CO_3} + \underset{\text{carbon}}{2C} = \underset{\substack{\text{carbon}\\\text{monoxide}}}{3CO} + \underset{\text{potassium}}{K_2}$$

The mixture is heated to whiteness in an iron retort, and the vapors are passed into a copper receiver. The potassium distils over and condenses in globules, still containing carbon in the form of charcoal. It is purified by redistillation in an iron retort, and is condensed in a copper receiver filled with naphtha.

The manufacture of potassium is a rather dangerous kind of business, owing to the formation of a very explosive compound of potassium and carbon monoxide, which has the composition $C_6O_6K_6$. It has been lately proposed to manufacture this metal by heating potassium hydroxide $KOH$ with magnesium, the potassium distilling off in the current of evolved hydrogen:

$$2KOH + 2Mg = 2MgO + H_2 + K_2$$

Potassium is a soft, brilliant, bluish-white metal, tarnishing instantly, however, in the air to a dull, grayish color. It must always be preserved under naphtha. It possesses a specific gravity of .865, becoming brittle at 0°, and at 62.5° melting to a liquid closely resembling mercury. From this it may be crystallized in tetragonal octahedrons. It may be distilled in hydrogen and gives a green vapor.

Thrown upon water, it at once decomposes it, evolving so much heat that the hydrogen, set free, takes fire and burns with a characteristic violet flame (see Experiment 1,

*Inorganic Chemistry*, Part 1). It unites actively with chlorine and with sulphur. Its spectrum is characterized by two sharply defined lines—one in the red, having a wave length of .0007680 millimeter, and the other in the violet, having a wave length of .0004045 millimeter. By means of this spectrum, as minute a quantity of potassium as one three-thousandth of a milligram may be detected with absolute certainty.

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## POTASSIUM OXIDES.

**47. Potassium Oxide** $K_2O$.—This compound is obtained by the direct oxidation of the metal, as when thin pieces of it are exposed to dry air, or probably when potassium hydroxide is heated with potassium, according to the equation:

$$2KOH + K_2 = 2K_2O + H_2$$

It is a grayish-white, deliquescent, and caustic substance, and unites energetically with water to again form the hydroxide.

A *tetroxide of potassium* $K_2O_4$ is formed when potassium is heated in an excess of oxygen, but little is known, so far, about this substance.

**48. Potassium Hydroxide** $KOH$.—Potassium hydroxide, or potassium hydrate, commonly known as *caustic potash*, is prepared by boiling 1 part of potassium carbonate with 12 parts of water, and gradually adding milk of lime to the boiling liquid. The lime combines with the carbonic acid, forming an insoluble carbonate, while the potassium hydroxide remains in solution:

$$\underset{\text{potassium carbonate}}{K_2CO_3} + \underset{\text{calcium hydrate}}{Ca(OH)_2} = \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{potassium hydroxide}}{2KOH}$$

When the decomposition is finished, the liquid is allowed to settle, and the clear solution decanted and rapidly evaporated. The residue is melted in a silver dish and poured out upon flat stone slabs.

This product, which is known as *potash by lime*, is, however,

impure, and by treating it with alcohol, which dissolves only the potassium hydroxide, it may be freed of lime and any salts of potassium it may possess—especially of the carbonate, which is formed by the absorption of carbon dioxide from the air during evaporation. The clear alcohol solution is decanted, and, after the alcohol has been expelled by distillation, the residue is evaporated to dryness and fused in a silver dish. It is known as *potash by alcohol.*

Potassium hydroxide, which is perfectly pure chemically, is frequently used in the laboratory, and is usually prepared by double decomposition between potassium sulphate and barium hydrate, the potassium-hydroxide solution being separated by decantation from the insoluble barium sulphate:

$$K_2SO_4 + Ba(OH)_2 = BaSO_4 + 2KOH$$

Recently fused potassium hydroxide occurs as opaque white fragments having a short fibrous fracture and a density of 2.1. It melts at red heat and volatilizes at whiteness; it is not decomposed by heat. When exposed to the air, it absorbs moisture as well as carbon dioxide from the atmosphere, and deliquesces. It is very soluble in water. A hydrate having the composition $KOH,2H_2O$ is deposited from its hot and very concentrated solution in rhombohedral crystals.

Potassium hydroxide is very caustic; it softens and partly destroys the skin, and is, for this reason, employed as a caustic in surgery. It shows the properties of an *alkali* in the highest degree; these are, its solubility in water, its power to neutralize the acids and to decompose a great number of metallic solutions, and its corrosive action on the tissues. This alkalinity may be shown by the energy with which the most feeble solutions of potassium hydroxide restore the blue color to reddened litmus.

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## SULPHIDES OF POTASSIUM.

**49.** Potassium is combustible in vapor of sulphur, and unites with it in five different proportions, forming the following compounds: $K_2S$, $K_2S_2$, $K_2S_3$, $K_2S_4$, and $K_2S_5$.

**50.** *Potassium sulphide* $K_2S$ is obtained as a red crystalline mass by heating potassium sulphate $K_2SO_4$ in hydrogen. It exists in the residue left by the explosion of gunpowder. Water decomposes it, so that it smells of $H_2S$ when exposed to air. A solution of $K_2S$ is prepared by saturating a solution of $KOH$ with $H_2S$, and adding another equal quantity of $KOH$. In the first operation $KSH$ is formed, which is converted into $K_2S$ on adding $KOH$. From the solution, crystals of $K_2S,5H_2O$ may be obtained.

**51.** *Potassium hydrosulphide* $KSH$ may be formed by displacing 1 atom of $H$ in $H_2S$ by $K$, or by heating $K_2CO_3$ to redness in $H_2S$, according to the equation:

$$K_2CO_3 + 2H_2S = 2KSH + H_2O + CO_2$$

It is a yellow solid, very soluble in water, and crystallizing as $2KSH,H_2O$. When exposed to air, the solution becomes yellow from the formation of potassium disulphide:

$$2KSH + O = K_2S_2 + H_2O$$

On longer exposure, the solution becomes colorless, potassium thiosulphate being formed:

$$K_2S_2 + 3O = K_2S_2O_3$$

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## POTASSIUM AND CHLORINE.

**52.** *Potassium chloride* $KCl$ constitutes the mineral sylvite. It is obtained commercially from sea-water, from kelp (the ash of seaweed), from the refuse of the manufacture of sugar from beet root, or from an abundant mineral of the Stassfurt mines, *carnallite*, which is potassio-magnesium chloride. It is a transparent, colorless solid which crystallizes in cubes; it has a specific gravity of 1.9 and has a bitter, salty taste. It is soluble in water and produces a depression of temperature in dissolving. One part of potassium chloride dissolves in 3 parts of water at 17.5°; 100 parts of water at 0° dissolve 29.23 grams of potassium chloride and .2738 gram additional for each degree rise in temperature.

## POTASSIUM AND IODINE.

**53.** Potassium iodide and bromide are commercially important on account of their use in medicine and photography.

*Potassium iodide* $KI$ is prepared on a large scale by the direct action of iodine on potassium hydrate:

$$\underset{\text{iodine}}{3I_2} + \underset{\text{potassium hydrate}}{6KOH} = \underset{\text{potassium iodide}}{5KI} + \underset{\text{potassium iodate}}{KIO_3} + \underset{\text{water}}{3H_2O}$$

Potassium iodide and iodate are formed, the latter being precipitated. The whole is evaporated to dryness, and the residue heated to redness, whereby the iodate is converted into iodide. The mass is dissolved in hot water; on cooling, the solution deposits the iodide in fine, colorless, and transparent crystals. 100 parts of water at 18° dissolve 143 parts of potassium iodide; it is also readily soluble in alcohol.

A solution of potassium iodide dissolves iodine readily.

*Potassium bromide* $KBr$ is quite similar in properties to the iodide, and is obtained by an analogous process. It crystallizes in cubes, which are soluble in about 1.5 parts of cold water.

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## SALTS OF POTASSIUM.

**54. Potassium Nitrate.**—Potassium nitrate $KNO_3$, long known as niter or saltpeter, is found in some parts of India, in Egypt, Persia, Hungary, Spain, etc., where it sometimes appears as a white incrustation on the surface of the soil and is sometimes mixed with the soil to some depth. The niter is extracted from the earth by treating the earth with water, and the solution is evaporated, at first by the heat of the sun, and afterwards by artificial heat, when the impure crystals are obtained, which are exported as *grough* (or impure) saltpeter.

Saltpeter is far less abundant in northern climates than in southern. It is formed wherever nitrogenized organic substances decompose in the presence of potassium hydrate.

It is also manufactured artificially by exposing to the air mixtures of animal matters with wood ashes and lime, moistened with stable drainings or stale urine.

The greater part of the saltpeter of commerce is now obtained from sodium nitrate, of which enormous deposits occur in Peru and Chile.

The conversion of this so called *Chile saltpeter* into potassium nitrate is effected in the following manner: The recrystallized sodium nitrate is dissolved in water, and an equivalent quantity of potassium chloride, which is abundantly obtained from the Stassfurt mines, is added. The solution is boiled down; the hot liquid deposits sodium chloride, which is separated, and potassium nitrate crystallizes out on cooling.

Potassium nitrate crystallizes from its aqueous solution in long, six-sided prisms, which have a cool and slightly bitter taste. It melts at 350°; at a higher temperature it disengages oxygen and is converted into *potassium nitrite* $KNO_2$, which in its turn is decomposed at a red heat, leaving a mixture of oxide and peroxide of potassium.

Potassium nitrate is very soluble in water, the solvent power of the water increasing as its temperature rises. While 100 parts of water at 0° dissolve only 13.33 parts, at 100° it dissolves 246 parts.

Potassium nitrate is largely used in the manufacture of gunpowder, which is an intimate mixture of niter, charcoal, and sulphur.

**55. Potassium Sulphate.**—Potassium sulphate $K_2SO_4$ is found in certain salt mines in the mineral *kainit* $K_2SO_4, MgSO_4, MgCl_2, 6Aq$. It is also largely obtained as a secondary product in various manufacturing processes. It deposits from the mother liquors of the soda from seaweed when these are exposed to low temperatures. It may be obtained by saturating, with potassium carbonate, the acid potassium sulphate formed in the preparation of nitric acid by the decomposition of potassium nitrate with sulphuric acid.

Potassium sulphate is soluble in about 10 parts of cold water, but in a much smaller quantity of boiling water; it has a bitter taste and is neutral to test paper. Its crystals are a combination of rhombic pyramids and prisms, resembling those of quartz in formation and appearance; they are anhydrous, and decrepitate when suddenly heated, which is often the case with anhydrous crystals, i. e., those containing no water of crystallization. They are insoluble in alcohol.

**56. Acid Potassium Sulphate.**—Acid potassium sulphate $KHSO_4$, commonly known as *bisulphate of potash*, may be prepared by mixing potassium sulphate with half its weight of concentrated sulphuric acid, and evaporating to dryness the mixture in a platinum vessel; the fused salt thus obtained is then dissolved in hot water and left to crystallize. The crystals are either rhombic octahedrons or tabular crystals belonging to the orthorhombic system.

They are much more soluble than the normal salts, requiring only twice their weight of water, having a temperature of 15.5° and half that quantity at 100°; the solution is acid and has a sour taste.

**57. Potassium Chlorate.**—Potassium chlorate $KClO_3$ is formed, together with potassium chloride, by the action of chlorine on a concentrated solution of potassium hydrate or carbonate; thus,

$$3Cl_2 + 6KOH = KClO_3 + 5KCl + 3H_2O$$

It is soluble in about 20 parts of cold and 2 parts of boiling water, the crystals are anhydrous, flat, and tabular, and in taste somewhat resemble niter.

In the arts, potassium chlorate is obtained by the action of chlorine on a mixture of lime, potassium chloride, and water, heated in closed vessels. Chlorate and chloride of calcium are formed, and in the presence of the potassium chloride a double decomposition takes place, potassium chlorate and calcium chloride, which latter is very soluble, being formed. The liquid is filtered hot, and the potassium chlorate crystallizes out on cooling:

$$KCl + 3CaO + 3Cl_2 = KClO_3 + 3CaCl_2$$

Potassium chlorate melts at 400°, and at a higher temperature is decomposed into oxygen and potassium chloride. Potassium chlorate deflagrates when thrown upon hot coals; when mixed with sulphur, it explodes by friction or percussion.

**58. Potassium Perchlorate.**—Potassium perchlorate $KClO_4$ is formed by the action of either heat or sulphuric acid on potassium chlorate. It is remarkable for its sparing solubility, for it requires 70 parts of cold water to dissolve it. It crystallizes in anhydrous and transparent right rhombic prisms, and above 400° decomposes into potassium chloride and oxygen.

**59. Potassium Neutral Carbonate.**—Potassium neutral carbonate $K_2CO_3$ is met in commerce under the name *potash*. It is obtained by lixiviating wood ashes, i. e., exhausting them with water, evaporating the solution to dryness, and calcining the residue in the air. The potash thus obtained is impure potassium carbonate, mixed with various other salts of potassium, such as the chloride, and sulphate, and silicate, and it only contains, approximately, from 60 to 80 per cent. of carbonate.

Potassium carbonate is now manufactured on a large scale from the native chloride, so called *Stassfurt salt*, by a process similar to that which will be described for the manufacture of sodium carbonate from common salt.

Neutral potassium carbonate is very soluble in water, and readily absorbs the moisture from the air; the solution is highly alkaline to test paper. It is insoluble in alcohol. This substance is largely employed for various purposes in the arts, and is a compound of considerable importance.

**60.** During the fermentation of the grape juice, in the preparation of wine, a hard crystalline substance is deposited, which is known in commerce by the name of *argol*, or, when purified, as *cream of tartar*. The chemical name of this salt

is *potassium bitartrate*, or *hydropotassium tartrate*, for it is derived from potash and tartaric acid, the latter being a vegetable acid having the composition $H_2C_4H_4O_6$. When this salt $KHC_4H_4O_6$ is heated, it leaves potassium carbonate mixed with carbon; but, if the heat is continued and free access of air permitted, the carbon will be entirely burned away, and potassium carbonate (salt of tartar) will be left.

In wine-producing countries, potassium carbonate is mostly prepared from the refuse yeast that rises during the fermentation, and is dried in the sun in order to be subsequently incinerated.

The fleece of sheep contains a considerable proportion of a salt of potassium with an animal acid; when the fleece is washed with water, this salt is dissolved out, and on evaporating the liquid and burning the residue, this is converted into potassium carbonate.

**61. Acid Potassium Carbonate.**—Acid potassium carbonate $KHCO_3$, or *bicarbonate of potash*, or *hydropotassium carbonate*, often sold as the neutral potassium carbonate, and used in medicine, is prepared by saturating moist $K_2CO_3$ with $CO_2$, or by passing $CO_2$ through a strong solution of $K_2CO_3$. It forms prismatic crystals that are much less alkaline and less soluble in water than is the neutral carbonate, into which they are converted by heat:

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

The aqueous solution of $KHCO_3$ gradually loses $CO_2$ when boiled.

**62. Potassium Phosphates.** — *Neutral orthophosphate* $K_3PO_4$, formed by igniting phosphoric acid with excess of potassium carbonate, is readily soluble in water and crystallizes in small needles. The *dipotassium salt* $K_2HPO_4$, obtained by mixing aqueous phosphoric acid with a quantity of carbonate of potassium sufficient to produce a slight alkaline reaction, and evaporating, is easily soluble in water, but does not crystallize. The *monopotassium salt* $KH_2PO_4$,

obtained by using a slight excess of phosphoric acid, forms small needle-shaped crystals, which are easily soluble in water, but insoluble in alcohol.

*Normal potassium pyrophosphate* $K_4P_2O_7$ is deliquescent, and separates from aqueous solution in fibrous crystals. The acid salt $K_2H_2P_2O_7$ separates as a deliquescent mass on adding alcohol to a solution of the normal pyrophosphate in acetic acid.

*Potassium monometaphosphate* $KPO_3$ is almost insoluble in water; the dimetaphosphate $K_2P_2O_6, H_2O$, prepared by decomposing the corresponding copper salt with potassium sulphide, is soluble in water and crystallizable; it is converted by ignition into the monometaphosphate.

**63. Potassium Arsenates.**—The *neutral salt* $K_3AsO_4$ is obtained by treating arsenic acid with an excess of potash. It is crystalline. The dipotassium salt $K_2HAsO_4$ is crystallized with difficulty. The monopotassium salt $KH_2AsO_4$ forms large crystals.

**64. Potassium Arsenites.**—The salt $KAsO_2, H_3AsO_3$ is obtained as a crystalline powder on adding alcohol to a solution of arsenious oxide in the minimum quantity of potash. This salt, when heated with a solution of potassium carbonate, is converted into the meta-arsenite $KAsO_2$, which in turn, when heated with caustic potash, yields the *diarsenite* $K_4As_2O_5$.

A solution of potassium arsenite, known in medicine as *Fowler's solution*, is prepared by boiling 1 part of arsenious oxide with 1 part of potassium carbonate in distilled water, and diluting to 90 parts of solution.

**65. Potassium Borates.**—The metaborate $KBO_2$ is obtained by fusing a mixture of boric acid and potassium carbonate; it is only slightly soluble in water and separates in small crystals.

It has an alkaline reaction and absorbs carbonic acid from

the air, being thereby converted into the *pyroborate* or *tetraborate* $K_2B_4O_7 = K_2O,2B_2O_3$. This latter, which is also formed on mixing a solution of boric acid with a slight excess of potash, is easily soluble, and crystallizes in hexagonal prisms containing $5H_2O$. The *triborate* $2KB_3O_5,5H_2O$, or $K_2O,3B_2O_3,5H_2O$, is formed on mixing the hot solution of boric acid and potassium carbonate, and separates in glittering rhombic crystals. The *pentaborate* $2KB_5O_8,4H_2O$, or $K_2O,5B_2O_3,4H_2O$, separates in rhombic octahedrons from a hot solution of caustic potash saturated with boric acid.

**66. Potassium Silicates.**—The *metasilicate* $K_2SiO_3$, or $K_2O,SiO_2$, is formed when silica is fused with an equivalent quantity of potassium carbonate, or with any larger quantity; for experiment shows that 1 molecule of silica cannot decompose more than 1 molecule of potassium carbonate; so that, for instance, the reaction $2(K_2O,CO_2)+SiO_2 = (K_2O)_2SiO_2+2CO_2$ cannot take place, and the orthosilicate $K_4SiO_4$ does not exist. The *tetrasilicate* $K_2Si_4O_9$ is prepared by fusing 45 parts of quartz, 30 parts of potash, and 3 parts of powdered charcoal, boiling the resulting grayish-black glassy mass with water, mixing the resulting concentrated solution with strong alcohol, and washing the precipitate thereby formed with cold water.

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## SODIUM.

*Symbol Na. Atomic weight 22.99. Valence I.*

**67. History and Occurrence.**—Though sodium oxide was already recognized in the year 1736 by Duhamel, the metal in the pure state was only obtained in 1807 by Sir Humphry Davy. Sodium does not occur in the free state in nature, but is found abundantly in combinations. Its chloride, or salt, is known as the mineral *halite*, and is found not only in immense deposits of rock salt, but also in enormous quantities in sea-water and in the waters of saline springs. Sodium also occurs in the form of nitrate, or soda niter; of borate, or borax; of carbonate, or trona; and of

silicate, in albite, oligoclase, sodalite, etc. It is found in marine plants, and is essential to animal life.

**68. Preparation and Properties.**—Sodium is prepared by distilling a mixture of sodium hydroxide and carbon at a temperature of about 800°, when the metal distils over, according to the equation:

$$6NaOH + 2C = 2Na_2CO_3 + Na_2 + 3H_2$$

It is usually prepared by reducing its oxide by carbon at a white heat; thus,

$$Na_2O + C = Na_2 + CO.$$

Practically, 30 kilograms of dry sodium carbonate, 13 kilograms of charcoal, and 3 kilograms of chalk are intimately mixed together, calcined, and introduced into iron cylinders heated in a reverberatory furnace. At a bright red heat the sodium distils over, and is collected in receivers. To purify it, it is redistilled, melted under petroleum, and cast into ingots, which are preserved under naphtha.

In *Castner's process* the fused sodium hydroxide is heated in steel crucibles (provided with covers in which condensing tubes are inserted) with a mixture of carbon and finely divided iron. The reduction of the sodium is effected by the carbon, the iron serving to keep the carbon down below the surface of, and therefore in direct contact with, the fused hydroxide. The residues in the crucibles are treated with warm water, and the solution evaporated to recover the sodium carbonate, while the iron is dried, and used over again. The distillation is carried on in a gas furnace, and is said to yield 90 per cent. of the sodium present.

Sodium is a lustrous, silver-white, soft metal; its specific gravity is .973, becoming brittle at −20°, melting at 95.6°, and boiling at 742°. It crystallizes in tetragonal octahedrons. On exposure to air it rapidly tarnishes, and, if thrown on water, decomposes it with effervescence; if it is prevented from moving, or if the water is warm, it takes fire, burning with a characteristic yellow flame, and yielding a spectrum consisting of a double yellow line with a wave length of

.0005892 millimeter. Sodium is far less costly than potassium, and is used on a large scale for the extraction of the metal magnesium, and for making sodium peroxide. An amalgam of sodium is also employed with advantage in extracting gold and silver from their ores.

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## COMPOUNDS OF SODIUM.

**69. Sodium Chloride.**—Sodium chloride $NaCl$ is common salt, or sea salt. It is widely diffused in nature, and is found in the solid state, as rock salt, in many countries. Sea-water contains a large proportion of sodium chloride, and it exists also in various mineral springs.

Sodium chloride may be formed by the direct union of its constituents, as by burning sodium in chlorine gas. It is obtained commercially by either mining it directly, in which form it is known as *rock salt*, or by evaporating either sea-water or the waters of saline springs, producing solar salt if the heat is natural, and boiled salt if artificial heat is employed.

Much of the salt of commerce is obtained by the evaporation of sea-water along the Mediterranean. The water is let into basins a few inches deep, which are continually swept by the summer winds. It thus becomes concentrated, and is kept in motion from one basin to another, until it arrives in the areas where the salt is deposited.

Extensive beds of rock salt occur in France, Germany, Hungary, Spain, Abyssinia, and Mexico. Perfectly pure specimens of rock salt form beautiful, colorless cubes, and are known as *sal gemme*, but ordinary rock salt is only partially transparent, and exhibits a rusty color, owing to the presence of iron.

At Droitwich, in Worcestershire, England, the salt is obtained by evaporation from the waters of certain saline springs. In some parts of France and Germany, the water from the salt springs contains so little salt that it would not pay for the fuel necessary to evaporate the water, and a very

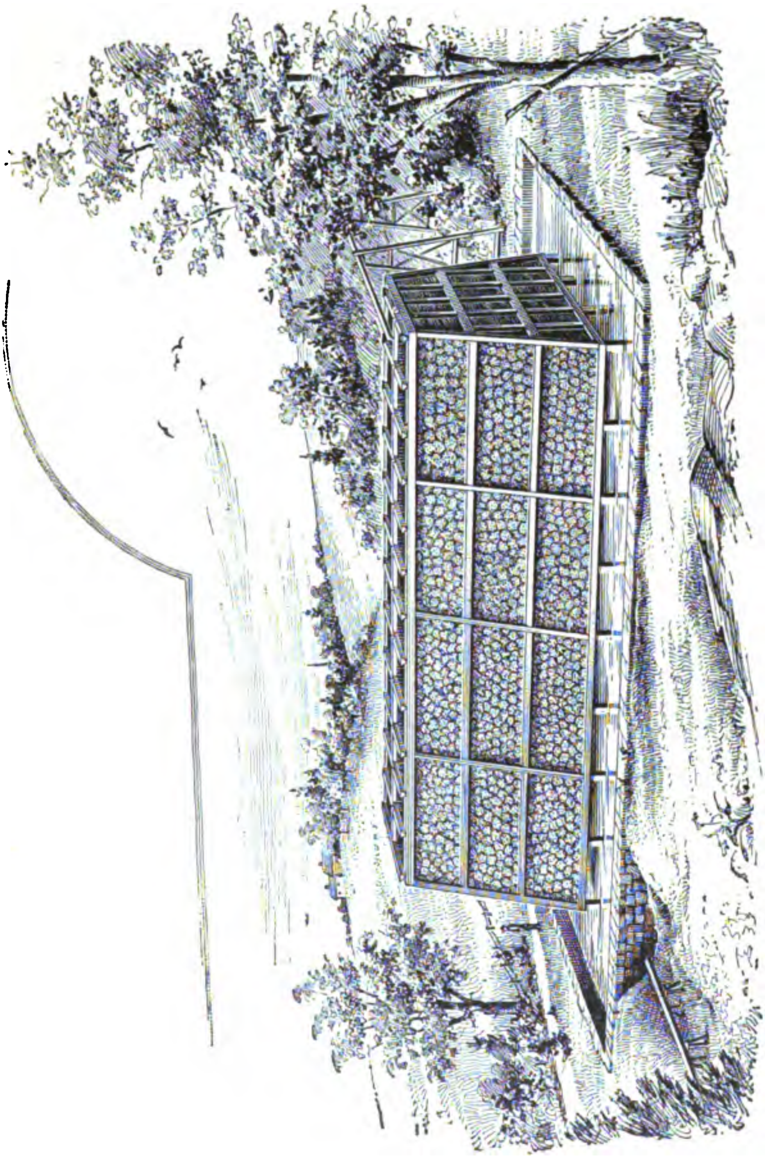

FIG. 8.

ingenious plan is adopted by which the proportion of water is greatly reduced without the application of artificial heat. For this purpose a lofty scaffolding is erected and filled with bundles of twigs and brushwood, over which the salt water is allowed to flow (see Fig. 3), having been raised to the top of the scaffolding by pumps. In trickling over the twigs and brushwood this water exposes a large surface to the action of the wind and the sun, and a considerable evaporation takes place, so that a much stronger brine is collected in the reservoir beneath the scaffolding; by several repetitions of the operation the proportion of water is so far diminished that the rest may be economically evaporated by artificial heat.

**70.** Sodium chloride is a colorless, transparent solid, which crystallizes from its aqueous solution in cubes. The crystals are generally very small; they are anhydrous and are nearly equally soluble in hot and cold water. According to Gay-Lussac,

1 part of common salt dissolves in 2.78 parts of water at 14°.
1 part of common salt dissolves in 2.7 parts of water at 60°.
1 part of common salt dissolves in 2.48 parts of water at 109.7°.

The saturated solution boils at 109.7°.

The great tendency observed in ordinary table salt to become damp when exposed to the air is due chiefly to the presence of small quantities of chlorides of magnesium and calcium, for pure sodium chloride has very little tendency to attract atmospheric moisture, although it is so easily dissolved by water.

**71. Sodium Oxides and Sodium Hydroxide.**—*Sodium oxide* $Na_2O$ may be obtained by the combustion of sodium in air; it is a white, fusible substance, uniting directly with water to form *sodium hydroxide* or *hydrate* $NaOH$. Sodium hydroxide, generally known as *caustic soda*, is frequently employed in the laboratory and in the arts. It is prepared, in the pure state, by the action of the metal on water; commercially, it is obtained by the action of calcium hydrate—

milk of lime—on sodium carbonate. The clear liquid thus obtained is evaporated in iron vessels, and the fused mass that is left is poured on to flat plates or cast in sticks. It is a white, opaque, and brittle solid of specific gravity 2. It is deliquescent and absorbs carbon dioxide from the air. It is freely soluble in water, and may be obtained crystallized in prisms having the composition $2NaOH, 7Aq$.

*Sodium dioxide*, or *sodium peroxide* $Na_2O_2$, is now produced on a commercial scale by heating sodium to 300° in a mixture of nitrogen and oxygen, in which the proportion of the latter is gradually increased. It is a yellowish substance, and acts as a powerful oxidizing agent. Water decomposes it into hydrogen dioxide and sodium hydroxide. It is chiefly applied in bleaching silk and wool.

**72. Sodium Sulphide and Sulphydrate.**—Sodium sulphide $Na_2S$ may be obtained in the following way: A concentrated solution of sodium hydrate is divided into two equal parts; one part is then saturated with hydrogen sulphide, sodium sulphydrate resulting according to the equation:

$$\underset{\text{sodium hydrate}}{NaOH} + \underset{\text{hydrogen sulphide}}{H_2S} = \underset{\text{sodium sulphydrate}}{NaSH} + \underset{\text{water}}{H_2O}$$

To this sodium sulphydrate the other portion of sodium hydrate is added, and the solution is concentrated out of contact with the air. Hydrated crystals of sodium sulphide are deposited.

$$\underset{\text{sodium sulphydrate}}{NaSH} + \underset{\text{sodium hydrate}}{NaOH} = \underset{\text{water}}{H_2O} + \underset{\text{sodium sulphide}}{Na_2S}$$

The crystals are rectangular prisms terminated by four-faced points. These crystals are very soluble in water, and should be colorless when pure.

**73. Sodium Sulphate.**—Sodium sulphate $Na_2SO_4$ is obtained abundantly commercially, as a residue in various chemical processes, as, for instance, in the preparation of

nitric and hydrochloric acid. It is also largely produced as an intermediate product in the manufacture of soda. It occurs native, anhydrous as *thenardite*, and hydrated as *mirabilite*. It crystallizes from solution in large, colorless prisms, which have the composition $Na_2SO_4,10Aq$, and which are efflorescent in dry air, losing all their water. The anhydrous salt is soluble in $2\frac{1}{2}$ parts of water at 100°.

**74. Acid Sodium Sulphate.**—Acid sodium sulphate, or hydrosodium sulphate $HNaSO_4$, is obtained by adding sulphuric acid to the neutral sulphate. On cooling the saturated solution, oblique rhombic prisms are obtained, which contain 2 molecules of water of crystallization. These crystals are very readily soluble in water, and have an acid taste. Alcohol decomposes them into sulphuric acid and neutral sulphate, which latter is precipitated.

**75. Sodium Carbonate.**—Sodium carbonate $Na_2CO_3$, one of the most widely used salts, generally known as *soda*, or *soda ash*, was for a long time prepared from barilla. Barilla is the commercial name of the ash obtained by burning a marine plant known as *Salsola;* but, as this ash contains only about 25 per cent. of carbonate of soda, its price was proportionately high, and those manufacturers to whom this salt was indispensable in their manufacturing processes were considerably fettered.

During the war that followed the French Revolution, the price of barilla, which was largely imported from Spain, had risen to such an extent that Napoleon Bonaparte, in order to help the industries of his country and to create new business, deemed it advisable to offer a prize for the discovery of a process by which carbonate of sodium could be produced at home.

To this circumstance we are indebted for a process, discovered by Le Blanc, by which sodium carbonate could be manufactured cheaply.

The process consists in heating salt and sulphuric acid, whereby sodium sulphate and hydrochloric acid are produced; thus,

$$\begin{array}{ccccccc} 2NaCl & + & H_2SO_4 & = & Na_2SO_4 & + & 2HCl \\ \text{salt} & & \text{sulphuric acid} & & \text{sodium sulphate} & & \text{hydrochloric acid} \end{array}$$

The sodium sulphate thus obtained, and technically known as *salt cake*, is mixed with coal and limestone and again heated to convert it into sodium carbonate, a process which may be represented by the following two equations:

$$\begin{array}{lccccccc} (1) & Na_2SO_4 & + & C_2 & = & Na_2S & + & 2CO_2 \\ & \text{sodium sulphate} & & \text{carbon} & & \text{sodium sulphide} & & \text{carbon dioxide} \\ (2) & Na_2S & + & CaCO_3 & = & Na_2CO_3 & + & CaS \\ & \text{sodium sulphide} & & \text{calcium carbonate} & & \text{sodium carbonate} & & \text{calcium sulphide} \end{array}$$

The resulting mixture of sodium carbonate and calcium sulphide, technically known as *black ash*—its color originating from the presence of coal—is mixed with water, which readily dissolves the sodium carbonate, leaving the calcium sulphide undissolved as so called *tank waste*. The water is evaporated and the sodium carbonate obtained as crystals.

From these outlines the actual process of manufacture employed will now be readily understood by the student.

In the first part of the process, which is known as the *salt-cake process*, equal parts of common salt and sulphuric acid

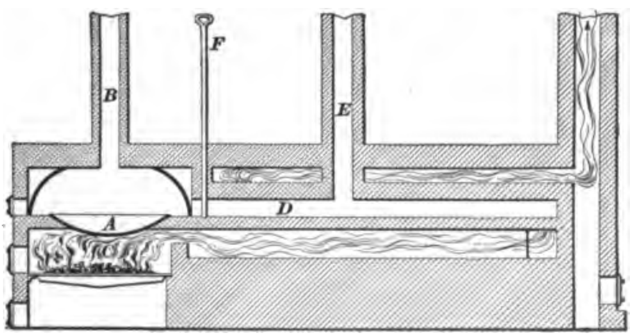


FIG. 4.

are mixed and heated in an iron pan *A* of a furnace shown in Fig. 4, by a fire in the grate *C*. The hydrochloric-acid

gas evolved rises and escapes through flue *B*, whence it passes to a brick tower filled with coke, down which a fine shower of water trickles. The entering hydrochloric-acid gas is readily absorbed by the water, forming with it the *muriatic acid* of commerce. From pan *A* the partly decomposed salt is transferred through the raised door *F* into a brick roaster *D*, which is virtually a muffle heated by the flames from the furnace, which circulates in the flues surrounding it. The conversion of the salt into sodium sulphate is here completed, the hydrochloric-acid gas still evolving, being allowed to escape through the flue *E* to condensing towers constructed similarly to the one previously described.

The second part of the process takes place in a reverberatory furnace, known as the *black-ash* furnace. In this furnace, a mixture of 10 parts of salt cake (sodium sulphate), 10 parts of limestone, and 4 to 6 parts of small coal are heated. To the black ash obtained, water is added, to dissolve the sodium carbonate; the solution is then drawn off, and, by the evaporation and calcination of the residue, ordinary crude soda is obtained. This soda is, however, far from being chemically pure, as it contains, in addition to a considerable amount of salt and sodium sulphate, a certain amount of caustic soda formed by the action of lime on the carbonate.

The crude soda ash is purified by mixing it with sawdust, and heating the mixture. The carbon dioxide formed by the heated sawdust converts the caustic soda into carbonate, and, by dissolving the mass in water and evaporating the solution, crystals of common washing soda, having the composition $Na_2CO_3,10H_2O$, are obtained.

The calcium sulphide, referred to as *tank waste*, is not wasted. It is converted, according to a process discovered by Chance, into marketable sulphur.

**76.** Another process, known as *Solvay's process*, or the *ammonia-soda process*, has lately entered into successful competition with the original Le Blanc process, and has, in fact, superseded it.

This process depends on the double decomposition which

takes place between sodium chloride and acid ammonium carbonate in concentrated aqueous solution:

$$NaCl + NH_4HCO_3 = NH_4Cl + NaHCO_3$$

The acid sodium carbonate, which is less soluble than ammonium chloride, is precipitated, and is collected and converted into the neutral carbonate by means of heat; thus,

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

It thus loses half its carbon dioxide, which is utilized for the preparation of a new quantity of acid ammonium carbonate. The other portion of the carbon dioxide necessary for this operation is produced by the calcination of limestone (calcium carbonate) which at the same time yields the lime necessary for the liberation of the ammonia contained in the mother liquor in the form of ammonium chloride.

**77.** A considerable quantity of sodium carbonate is also produced from cryolite, which is a double fluoride of sodium and aluminum, and of which large deposits exist in Greenland.

This mineral is calcined with lime, calcium fluoride and aluminate of soda being formed, according to the equation:

$$\underset{\text{cryolite}}{2(AlF_3, 3NaF)} + \underset{\text{calcium oxide}}{6CaO} = \underset{\text{calcium fluoride}}{6CaF_2} + \underset{\text{sodium aluminate}}{Al_2O_3, 3Na_2O}$$

The latter compound is dissolved out by water and decomposed by carbon dioxide, aluminum hydroxide being precipitated and sodium carbonate remaining in solution.

**78.** The crystals of sodium carbonate are easily distinguished by their property of efflorescing in dry air, and by their alkaline taste, which is much milder than that of potassium carbonate, which is a deliquescent salt. The crystals are very soluble in water, and the solution possesses a strong alkaline reaction. The solubility of sodium carbonate is well illustrated by the subjoined data:

100 parts of water at 0° dissolve 7.08 parts of sodium carbonate.
100 parts of water at 10° dissolve 16.06 parts of sodium carbonate.
100 parts of water at 20° dissolve 25.93 parts of sodium carbonate.
100 parts of water at 25° dissolve 30.83 parts of sodium carbonate.
100 parts of water at 30° dissolve 35.90 parts of sodium carbonate.
100 parts of water at 104.6° dissolve 48.50 parts of sodium carbonate.

The saturated solution boils at 104.6°. Sodium carbonate is insoluble in alcohol.

**79. Acid Sodium Carbonate.**—Acid sodium carbonate, hydrogen-sodium carbonate, or bicarbonate of soda $NaHCO_3$, is the substance commonly used in medicine as carbonate of soda. It is prepared either by saturating crystallized sodium carbonate with $CO_2$ or by passing $CO_2$ through a strong solution of common salt mixed with ammonia. It forms small four-sided crystals much less easily dissolved by water than the carbonate. The taste of the solution is salty, and much less alkaline than that of carbonate of sodium. The solution of bicarbonate of soda evolves $CO_2$ when heated, and crystals of the *sesquicarbonate* $Na_2CO_3, NaHCO_3, 2Aq$ may be obtained from it.

**80. Phosphates of Sodium.**—Three phosphates of sodium are obtained from phosphoric acid:

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\} PO_4$$

phosphoric acid

$$\left.\begin{matrix}Na\\H\\H\end{matrix}\right\} PO_4 + 2H_2O$$

monosodium phosphate or dihydro-sodium phosphate

$$\left.\begin{matrix}Na\\Na\\H\end{matrix}\right\} PO_4 + 12H_2O$$

disodium phosphate or hydro-disodium phosphate

$$\left.\begin{matrix}Na\\Na\\Na\end{matrix}\right\} PO_4 + 12H_2O$$

trisodium phosphate or normal sodium phosphate

While monosodium phosphate exerts an acid reaction, the disodium and trisodium phosphates have an alkaline reaction. The most important in the arts and in commerce is disodium phosphate $Na_2HPO_4$. It crystallizes in prisms having the

composition $Na_2HPO_4, 12Aq$, which effloresce in air and readily dissolve in water, giving an alkaline solution. When heated, these crystals fuse easily, and lose the $12Aq$ at 45°; at a red heat they are decomposed into water and pyrophosphate, according to the equation:

$$\underset{\text{disodium phosphate}}{2Na_2HPO_4} = \underset{\text{water}}{H_2O} + \underset{\text{sodium pyrophosphate}}{Na_4P_2O_7}$$

$Na_2HPO_4$ occurs in the blood and in urine. It is prepared by decomposing with $H_2SO_4$ a mineral phosphate containing $Ca_3(PO_4)_2$, so as to obtain the insoluble $CaSO_4$ and a solution of impure $H_3PO_4$. This is decomposed by $Na_2CO_3$; the solution is filtered from the small quantity of $CaCO_3$ formed and crystallized:

$$H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + H_2O + CO_2$$

**81. Arsenate of Soda.**—Arsenate of soda, or disodium arsenate $HNa_2AsO_4$, forms crystals with $12Aq$, resembling those of the corresponding phosphate, but the salt, as it is usually sold, contains only $7Aq$.

Sodium arsenate is made by dissolving white arsenic in caustic soda, adding sodium nitrate, evaporating to dryness, heating the residue to redness, and dissolving in water:

(1) $$As_4O_6 + 12NaOH = 4Na_3AsO_3 + 6H_2O$$

(2) $$Na_3AsO_3 + NaNO_3 = Na_3AsO_4 + NaNO_2$$

(3) $$Na_3AsO_4 + H_2O = Na_2HAsO_4 + NaOH$$

**82. Sodium Borate.**—As has been previously stated, sodium borate, or *biborate of soda* $Na_2B_4O_7$—better known as *borax*—is deposited during the evaporation of the waters of certain lakes in Thibet, whence it is exported in impure crystals which are covered with a peculiar greasy coating. Borax is also found in certain lakes in California, and large quantities are now derived from the native borates of calcium and magnesium, such as *colemanite*, *borocalcite*, and *boracite*, which yield borax by a double decomposition with sodium carbonate.

When a concentrated boiling solution of borax is allowed to cool, it deposits, between 60° and 70°, octahedral crystals having the composition $Na_2B_4O_7, 5Aq$, while the crystals deposited below 60° are rhombic prisms containing 10 molecules of water. The latter form is that found in commerce. Borax solution is faintly alkaline.

The borax of commerce soon effloresces and becomes opaque when exposed to air, and while it may be easily distinguished by its alkaline taste and behavior, it is most readily recognized when heated. The crystals of borax fuse easily and swell up to a white, spongy mass of many times their original volume; this mass afterwards fuses down to a clear liquid, which forms, on cooling, a glassy mass, known as *vitrified borax*. Since this glass is capable of dissolving many metallic oxides with great readiness, it finds wide employment in the metallurgical arts. Large quantities of borax are used in potteries for glazing stoneware, etc. Borax possesses antiseptic properties, and is sometimes used as a preservative.

**83. Sodium Nitrate.**—Sodium nitrate $NaNO_3$ is imported from Chile and Peru under the name of *Chile saltpeter* or *cubic niter*. It is found in Tarapaca, in Chile, in enormous quantities. It is used as an artificial manure for supplying nitrogen to the soil, and for the manufacture of potassium nitrate and nitric acid.

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## AMMONIUM.

*Symbol Am. Formula $NH_4$. Valence I. Molecular weight 18.01.*

**84. History.**—The salts that ammonia forms by direct union show a great similarity to those formed by the metals potassium and sodium. To account for this remarkable similarity, Berzelius, in 1816, basing his ideas on a theory of Ampére, proposed to consider these salts as compounds of ammonium, a compound radical $(N^vH_4)'$ capable of acting

like the monad metals sodium and potassium. Being an unsaturated compound, ammonium, if it exists free, must have the formula $(N^vH_4)$ $(N^vH_4)$, or, in other words, must exist as a double molecule with the formula $N_2H_8$. Weyl, by condensing ammonia gas in the presence of sodium, obtained a bright blue, metallic-like liquid, which he assumed to be *sodammonium*, and to which he ascribed the formula $N_2H_6Na_2$. By acting on ammonium chloride with it, a similar blue liquid was obtained, which he considered to be free ammonium. Moreover, when mercury containing 1 per cent. of sodium is placed in a saturated solution of ammonium chloride, it increases considerably in bulk, becoming a pasty mass, which is the so called *ammonium amalgam.*

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## COMPOUNDS OF AMMONIUM.

**85. Ammonium Nitrate.**—Ammonium nitrate $NH_4NO_3$ is prepared by saturating nitric acid with ammonia. It crystallizes in large, transparent, fusible prisms, which are soluble in water and produce a notable depression of temperature in the act of solution, extending even to $-15°$. At 300°, ammonium nitrate is decomposed into nitrogen monoxide (hyponitrous oxide) and water, according to the equation:

$$\underset{\substack{\text{ammonium}\\\text{nitrate}}}{NH_4NO_3} = \underset{\text{water}}{2H_2O} + \underset{\substack{\text{hyponitrous}\\\text{oxide}}}{N_2O}$$

Ammonium nitrate is, as has been previously mentioned, and as is seen from the above equation, generally used for the preparation of *laughing gas.*

**86. Ammonium Nitrite.**—Ammonium nitrite $NH_4NO_2$ is interesting on account of its easy decomposition by heat:

$$NH_4NO_2 = N_2 + 2H_2O$$

This decomposition takes place on even boiling the solution, so that a mixture of solutions of potassium nitrite and ammonium chloride is used for preparing nitrogen. Ammonium nitrite is found in small quantities in rain water; it can

also be detected in the water condensed from hydrogen burning in the air. Ammonia is partly converted into this salt when oxidized by ozone or even by air in the presence of heated platinum:

$$2NH_3 + O_2 = NH_4NO_2 + H_2O$$

**87. Ammonium Carbonate.**—Ammonium carbonate, better known as *smelling salts*, or *Preston salts*, finds considerable employment in medicine, and is also largely used by bakers and confectioners for imparting lightness and sponginess to cakes, pie crusts, etc. It is usually prepared by mixing ammonium sulphate with twice its weight of chalk, and distilling the mixture in an iron or earthen retort, which communicates through an iron pipe with a leaden receiver, in which the ammonium carbonate collects as a transparent, fibrous mass and which is purified by resubliming it in iron vessels surmounted by leaden domes. The action of calcium carbonate on ammonium sulphate would be expected to furnish the normal carbonate $(NH_4)_2CO_3$, but this salt (even if produced) is decomposed by the heat employed in the process into *hydrogen ammonium carbonate*,

$$CO(ONH_4)(ONH_4) = CO(ONH_4)(OH) + NH_3$$

and *ammonium carbamate*,

$$CO(ONH_4)(ONH_4) = CO(ONH_4)(NH_2) + H_2O$$

The commercial carbonate is usually a mixture of 2 molecules of the former to 1 of the latter. By treating it with strong alcohol, the *carbamate* is dissolved and the hydrogen ammonium carbonate left.

When exposed to the air, it smells of ammonia, and gradually becomes

$$NH_4HCO_3 = [CO(ONH_4)(OH)]$$

the carbamate being decomposed and volatilized:

$$CO(ONH_4)(NH_2) = CO_2 + 2NH_3$$

On treating the commercial carbonate with a little water, the hydrogen ammonium carbonate is left undissolved,

while the carbamate is converted into normal carbonate and dissolved:

$$CO(ONH_4)(NH_2) + H_2O = (NH_4)_2CO_3$$

*Sal volatile* is an alcoholic solution of ammonium carbonate and carbamate.

**88.** Ammonium carbonate $(NH_4)_2CO_3$ is obtained in crystals by treating the commercial carbonate with strong ammonia. These crystals contain 10 molecules of water, and are deliquescent in air, evolving $NH_3$ and thus becoming converted into the bicarbonate, according to the equation:

$$(NH_4)_2CO_3 = NH_3 + NH_4HCO_3$$

**89. Ammonium Bicarbonate.**—Ammonium bicarbonate, or hydrogen-ammonium carbonate $NH_4HCO_3$, is the most stable of the carbonates of ammonium, and is obtained by dissolving the commercial carbonate in a little boiling water, when it crystallizes on cooling.

**90. Ammonium Carbamate.**—Ammonium carbamate is obtained as a white solid when ammonia gas is mixed with carbon dioxide, unless both are quite dry. It may be obtained in crystals by passing $CO_2$ and $NH_3$ into the strongest solution of ammonia.

Ammonium carbamate is easily soluble in water, which soon converts it into ammonium carbonate. The aqueous solution, when freshly prepared, is not precipitated by calcium chloride, but the calcium carbonate is deposited on standing or heating. When ammonium carbamate is heated in a sealed tube at 130°, it is decomposed into ammonium carbonate and urea*:

$$2(NH_4CO_2NH_2) = (NH_4)_2CO_3 + COH_4N_2*$$

*Carbamic acid* $HCO_2NH_2$ has not yet been isolated; its relation to carbonic acid is readily seen by a comparison of their formulas: carbonic acid, $COOHOH$; carbamic acid,

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*Urea, a colorless crystalline compound having the composition $COH_4N_2$, will be discussed in *Organic Chemistry*.

$COOHNH_2$. Other carbamates have been obtained by passing $CO_2$ through strongly ammoniacal solutions of different bases, and precipitating the carbamates by alcohol.

Carbamates are remarkable for evolving nitrogen when treated with a mixture of soda and sodium hypobromite; thus,

$$2(CONH_2ONa) + 3NaOBr + 2NaOH$$
$$= 2CO(ONa)_2 + 3NaBr + 3H_2O + N_2$$

If a solution of sodium carbamate is mixed with sodium hypochlorite and soda, no nitrogen is evolved until a soluble bromide is added, a reaction that will indicate bromides even in dilute solutions. The solution of sodium carbamate may be prepared by dissolving ammonium carbamate in a strong solution of soda, and allowing the mixture to stand over strong sulphuric acid under a bell jar for a day or two.

**91. Ammonium Sulphate.**—Ammonium sulphate $(NH_4)_2SO_4$ is obtained in the arts by passing into dilute sulphuric acid the ammonia that is disengaged when gas liquor is heated with lime. It crystallizes in right rhombic prisms. It is colorless and has a sharp taste. It dissolves in two parts of cold water and in its own weight of boiling water. It is insoluble in alcohol. Ammonium sulphate is manufactured on an extensive scale, and is used as a fertilizer.

**92. Ammonium Chloride.**—Ammonium chloride $NH_4Cl$ was formerly obtained from Egypt, where it was made by subliming the soot produced by the combustion of camel's dung. It is now produced on a large scale from gas liquor, or the water condensed in the manufacture of illuminating gas from coal. This liquor is heated with lime; ammonia is disengaged and is conducted into hydrochloric acid. Ammonium chloride is obtained by simply evaporating the solution. It is then purified by sublimation in stoneware pots, which are heated in a furnace out of which the upper parts of the pots project. The volatilized chloride condenses, and the sublimed product is known in trade as *sal ammoniac*, or *muriate of ammonia*.

It generally occurs as a white or grayish compact mass (having a crystalline fibrous structure), which is often striped with brown, owing to the presence of a little iron. It has a sharp and salty taste. It dissolves in 2½ parts of cold water, and in its own weight of boiling water. It is deposited from a saturated solution in small octahedral crystals, grouped together in needles, which thus present a fern-leaf appearance. At a high temperature it volatilizes without melting.

**93. Ammonium Sulphide.**—Ammonium sulphide, or hydrosulphate of ammonia $(NH_4)_2S$, has been obtained in colorless crystals by mixing hydrosulphuric-acid gas with twice its volume of ammonia gas in a vessel cooled by a mixture of salt and ice. It is a rather unstable compound, decomposing at the ordinary temperature in the air into free ammonia and *ammonium hydrosulphide* $NH_4HS$, which may be obtained in very volatile colorless needles by passing equal volumes of $NH_3$ and $H_2S$ into a vessel cooled in ice, or by passing hydrogen-sulphide gas into an alcoholic solution of ammonia, when it is obtained in colorless crystals, which, on vaporizing, dissociate into $NH_3$ and $H_2S$.*

When a strong solution of ammonia is saturated with hydrogen sulphide at 0°, a colorless solution is formed, from which colorless crystals of $NH_4HS$ separate. The solution soon becomes yellow in contact with the air, from the formation of *ammonium polysulphides* of the form $(NH_4)_2S_x$; eventually, the solution deposits sulphur and becomes colorless—thiosulphate, sulphite, and sulphate of ammonia being formed. When the freshly prepared colorless solution of ammonium hydrosulphide is mixed with an acid, the solution remains clear, hydrosulphuric acid being evolved with effervescence:

$$NH_4HS + HCl = NH_4Cl + H_2S$$

* A solution of ammonium sulphide, prepared by mixing the hydrosulphide (made by saturating ammonia solution with $H_2S$) with an equal volume of ammonia, is much used in analytical chemistry, and is supposed to contain $(NH_4)_2S$. The solution has a very disagreeable smell.

If, however, the solution has become already yellow, a milky precipitate of sulphur is produced, from the decomposition of the polysulphides, one of which is probably ammonium disulphide $(NH_4)_2S_2$.

The fresh solution gives a black precipitate of lead sulphide when a solution of lead acetate is added to it, but, after it has been kept till it is of a dark yellow or even red color, it gives a red precipitate of the persulphide of lead.

**94.** Ammonium polysulphides are the chief constituents of *Boyle's fuming liquor*, a disagreeably smelling yellow liquid obtained by distilling sal ammoniac with sulphur and lime. The polysulphides are frequently deposited in yellow crystals from this liquid. By dissolving sulphur in ammonium disulphide, orange-yellow prismatic crystals of *ammonium pentasulphide* $(NH_4)_2S_5$ may be obtained.

**95. Ammonium bromide** $NH_4Br$ and **ammonium iodide** $NH_4I$ are both largely employed in photography. Both are colorless crystalline salts, though ammonium iodide is very liable to become yellow and even brown, from the separation of iodine, unless it is kept in a dark and perfectly dry place, as ammonium iodide easily decomposes by the influence of the light, and is extremely soluble in water. Ammonium bromide is also very soluble in water.

**96. Hydrogen-sodium-ammonium phosphate, or microcosmic salt** $HNaNH_4PO_4,4Aq$, is found in putrid urine and guano. It may be prepared by mixing hot strong solutions of ammonium chloride and sodium phosphate, the reaction being expressed by the subjoined equation:

$$Na_2HPO_4 + NH_4Cl = HNaNH_4PO_4 + NaCl$$

It forms prismatic crystals that are very soluble and fusible, boiling violently when further heated, and finally leaving a transparent glass of sodium metaphosphate, which is valuable in blowpipe work for dissolving metallic oxides:

$$HNaNH_4PO_4 = NH_3 + H_2O + NaPO_3$$

## LITHIUM.

*Symbol Li. Atomic weight 7.01. Valence I.*

**97. History and Occurrence.**—Lithium oxide was recognized first as a new substance by Arfvedson, a Swedish chemist, in 1817. The metal was first prepared pure by Bunsen and Matthiessen in 1855. Lithium is a comparatively rare metal, being found principally in the rare minerals *amblygonite*, *spodumene*, *petalite*, *lepidolite*, and *triphylite*. The water of a number of mineral springs, both in this country and Europe, contains lithium in considerable quantity; traces of lithium have further been detected by means of the spectroscope in sea-water, in many minerals and meteorites, as well as in tobacco ash and various plants.

**98. Preparation and Properties.**—Metallic lithium is best obtained by the electrolysis of lithium chloride. It is a brilliant, silver-white metal, and somewhat softer than lead. It is remarkable as the lightest of the metals, having a specific gravity of only .578. It melts at 180° and burns in the air with an intense white flame when more strongly heated. It bears a general resemblance to potassium and sodium, but it is harder and less easily oxidized than those two metals. It decomposes water rapidly at ordinary temperatures, but does not burn upon it.

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## COMPOUNDS OF LITHIUM.

**99.** The compounds of lithium are *lithium chloride* $LiCl$, a deliquescent, fusible, and volatile salt; the *oxide* $Li_2O$, and the *hydroxide* $Li(OH)$, the latter a caustic, strongly alkaline substance; the *carbonate* $Li_2CO_3$; the *sulphate* $Li_2SO_4$; and the *phosphate* $Li_3PO_4$—all of which are well defined salts.

Lithium carbonate is occasionally employed medicinally. It is made from lepidolite by fusing the mineral, crushing it to powder, boiling with $HCl$ and $HNO_3$, and precipitating

the iron, lime, etc. by $Na_2CO_3$. The filtrate contains $NaCl$, $KCl$, and $LiCl$; it is concentrated and mixed with $Na_2CO_3$ to precipitate the $Li_2CO_3$.

The spectrum of lithium is characterized by an intense crimson line having a wave length of .0006705 millimeter, and a faint reddish-yellow line.

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## RUBIDIUM.

*Symbol Rb. Atomic weight 85.2. Valence I.*

**100. Preparation and Properties.**—Rubidium was first detected in the water of the Dürkheim Spring, in Germany, by Bunsen, in 1860, by means of the spectroscope. Its spectrum contains two characteristic dark-red lines, whence its name, which is derived from the Latin word *rubidus*, meaning "dark red."

This metal has since been found in small quantities in other mineral waters, and in the mineral lepidolite, as well as in the ashes of various plants.

By distilling the carbonate with charcoal, rubidium is obtained as a soft, white metal, of specific gravity 1.52. It melts at 38.5° and volatilizes below a red heat. It is more easily oxidized than potassium, to which it is closely related. It burns on water with exactly the same flame as potassium.

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## COMPOUNDS OF RUBIDIUM.

**101.** The salts of rubidium resemble closely those formed by potassium. The *chloride* crystallizes in cubes, dissolves in its own weight of water at 150°, and forms a double salt with platinum chloride. The *nitrate* $RbNO_3$ resembles saltpeter in its properties, but crystallizes in hexagonal prisms. The *carbonate* $Rb_2CO_3$ is an alkaline deliquescent salt. The *sulphate* $Rb_2SO_4$ is isomorphous with potassium sulphate.

## CÆSIUM.

*Symbol Cs. Atomic weight 133.0* (?). *Valence I.*

**102. History and Preparation.**—Cæsium was discovered simultaneously with rubidium, and in the same mineral water. Its name is derived from the Latin word *cæsius*, meaning "sky blue," and has reference to the two bright-blue lines which appear in its spectrum. The Dürkheim water contains in 5 kilograms scarcely 1 milligram of cæsium, but the mineral *lepidolite* of Hebron, Maine; contains .3 per cent. of cæsium; and the rare mineral *pollux*, found in the island of Elba, and resembling feldspar in composition, is said to contain a rather large percentage of this metal. The alum of the island of Vulcano is mentioned as a rich source of this metal, as well as of rubidium.

Metallic cæsium was obtained by Setterberg, in 1882, by electrolyzing a mixture of 4 parts of cæsium cyanide and 1 part of barium cyanide. It is a soft metal resembling silver in color, and has a specific gravity of 1.88. It fuses between 26° and 27°. The salts of cæsium closely resemble those of rubidium.

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## GENERAL REVIEW OF THE GROUP OF ALKALI METALS.

**103.** Cæsium, rubidium, potassium, sodium, and lithium constitute a group of elements conspicuous for their highly electropositive character, the powerfully alkaline nature of their hydroxides, and the general solubility of their salts. Their chemical characters and functions are directly opposite to those of the electronegative group embracing fluorine, chlorine, bromine, and iodine; and, like those elements, they exhibit a gradation of properties. Thus, cæsium appears to be the most highly electropositive member, rubidium the next, then potassium and sodium, while lithium is the least electropositive; and, just as iodine, the least electronegative of the halogen group, possesses the highest atomic number, so cæsium, the least electronegative (or most electropositive) of the alkali metals, has a higher atomic weight than any

other member of this group, their atomic weights being represented as follows: cæsium, 133; rubidium, 85.2; potassium, 39.04; sodium, 22.99; lithium, 7.01.

As in the case of the halogens, also, these are all univalent elements. Just as chlorine is accepted as the representative of *chlorous radicals*, so potassium is commonly regarded as the type of *basylous radicals*, the term *radical* being applied to all substances, whether elementary or compound, that are capable of being transferred, like chlorine or potassium, from one compound to another without suffering decomposition.

Attention has been called (see Arts. **42–44**) to the gradation exhibited in some of the physical properties of these elements. In some of their salts a similar gradational relation may be observed; the carbonates, for instance, of cæsium, rubidium, and potassium are highly deliquescent, absorbing water greedily from the air, while carbonate of sodium is not deliquescent, and carbonate of lithium is only sparingly soluble in water. The difficult solubility of the carbonate and phosphate of lithium constitutes the connecting link between this and the succeeding group of metals, the carbonates and phosphates of which are insoluble in water.

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## BARIUM.

*Symbol Ba. Atomic weight 136.8. Valence II.*

**104. History and Occurrence.**—Barium was first recognized as a new element by Scheele in 1774. Davy, in 1808, succeeded in isolating the metal. It gets its name from the great weight of its compounds, barium being derived from the Greek *βαρύς*, *barys*, meaning "heavy."

Barium is found in the North of England in two minerals known as *witherite* (barium carbonate $BaCO_3$) and *heavy spar*, or *barytes* (barium sulphate $BaSO_4$). Witherite, especially, is found in large masses in the lead mines at Alston Moor, Cumberland, and at Anglesark, Lancashire, England.

**105. Preparation and Properties.**—This metal is obtained by the electrolysis of fused barium chloride. It is a pale-yellow, lustrous, malleable metal of specific gravity 4, is easily oxidized by air, and rapidly decomposes water at ordinary temperatures. It requires a very high temperature to fuse it. Barium and its salts impart a green color to a flame.

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## COMPOUNDS OF BARIUM.

**106. Barium Oxide.**—Barium oxide, or *baryta* $BaO$, is obtained by strongly heating a mixture of barium carbonate and charcoal, according to the equation:

$$BaCO_3 + C = BaO + 2CO$$

It is a heavy, gray, porous solid, uniting energetically with water, and accompanied in its action by a hissing sound and the evolution of much steam. The product of the reaction, known as caustic baryta, is the hydrate or hydroxide $Ba(OH)_2$, which is obtained according to the following equation:

$$\underset{\text{barium oxide}}{BaO} + \underset{\text{water}}{H_2O} = \underset{\text{barium hydrate}}{Ba(OH)_2}$$

Barium hydrate is soluble in 2 parts of boiling water, and on cooling is deposited in large tabular crystals. The solution of barium hydrate in water is known as *baryta water.*

Crystallized barium hydrate may be produced by adding 113 grams of powdered barium nitrate to 340 cubic centimeters of a boiling solution of $NaOH$ containing 85 grams of commercial caustic soda in 567 cubic centimeters of water; the solution becomes turbid from the separation of barium carbonate produced from the sodium carbonate in the hydroxide; it is boiled for some minutes and then filtered; on partial cooling, some crystals of undecomposed barium nitrate are deposited; and, if the clear liquid is poured off into another vessel and stirred, it deposits an abundant mass of crystals of barium hydrate, having the composition

$Ba(OH)_2,8Aq$. These crystals soon effloresce and become opaque when exposed to the air.

**107. Barium Dioxide.**—Barium dioxide or peroxide $BaO_2$ is obtained by passing dry oxygen over barium oxide heated to dull redness. It is a gray, sometimes greenish-looking, porous substance. It loses its second atom of oxygen when heated to bright redness.

**108. Barium Sulphide.**—Barium sulphide $BaS$ is obtained by reducing barium sulphate with charcoal, according to the equation:

$$BaSO_4 + 4C = BaS + 4CO$$

The sulphate is ground to a fine powder and is mixed with flour. The mixture is then made into a thick paste by adding linseed oil, and is formed into little balls. These are calcined at a bright-red heat in a covered crucible, and a porous gray mass is thus obtained, which, when treated with boiling water, yields a solution that deposits hexagonal tablets after filtration and cooling. These crystals do not present a very constant composition, and their solution has a light-yellow color.

**109. Barium Chloride.**—Barium chloride $BaCl_2,2H_2O$ is the barium compound mostly used in the laboratory; it may be obtained by saturating the solution of barium sulphide with hydrochloric acid. Hydrogen sulphide is disengaged; the solution is boiled, filtered, and evaporated to crystallization. Barium chloride is deposited in tabular crystals, belonging to the type of the orthorhombic prisms, which are unaltered in the air. Barium chloride is easily soluble in water, but insoluble in alcohol, as well as in strong acids.

**110. Barium Chlorate.**—Barium chlorate $Ba(ClO_3)_2$ is employed in pyrotechnics, being prepared for that purpose by dissolving barium carbonate in a solution of chloric acid;

it forms beautiful, shining, tabular crystals. When mixed with combustible substances, such as charcoal and sulphur, it imparts a brilliant green color to the flame of the burning mixture.

**111. Barium Nitrate.**—Barium nitrate $Ba(NO_3)_2$ is prepared by decomposing barium sulphide with dilute nitric acid, filtering and evaporating the solution.

Barium nitrate crystallizes in regular octahedrons, the crystals being transparent and unaltered in the air. One part of barium nitrate requires for its solution about 20 parts of water at 12°, 5 parts of water at 15°, and 2.8 parts at 106°. When heated to redness, barium nitrate gives off oxygen, nitrogen, and red vapors, leaving a residue of $BaO$.

**112. Barium Sulphate.**—Barium sulphate $BaSO_4$, found abundantly in nature as heavy spar, has the specific gravity of 4.5. It is entirely insoluble in water and acids, except in concentrated sulphuric acid, where the solution, on cooling, deposits crystals of acid barium sulphate $BaH_2(SO_4)_2$.

*Artificial barium sulphate*, which is used by painters instead of white lead, under the name of *permanent white* (blanc fixe), and which is employed for glazing paper, cards, etc., is prepared by mixing the solution of barium sulphide with dilute sulphuric acid, when the barium sulphate separates as a white precipitate, which is collected, washed, and dried:

$$BaS + H_2SO_4 = H_2S + BaSO_4$$

**113. Barium Carbonate.**—Barium carbonate $BaCO_3$ occurs abundantly as the mineral *witherite*, and is found in orthorhombic prisms. It may be prepared by precipitating barium chloride with sodium carbonate. It is very insoluble in water, and is not decomposed by a red heat.

The artificial barium carbonate, which is used in the manufacture of some kinds of glass, is prepared by passing carbon dioxide through a solution of barium sulphide, when the carbonate is precipitated:

$$BaS + H_2O + CO_2 = H_2S + BaCO_3$$

**114.** In preparing compounds of barium from heavy spar (barium sulphate) on a small scale, it is advisable to convert the sulphate into barium carbonate. 50 grams of finely powdered barium sulphate are mixed with 100 grams of dried sodium carbonate, 600 grams of powdered niter, and 100 grams of very finely powdered charcoal. The mixture is placed in a heap on an iron plate, and is kindled with a match, when the heat, evolved by the combustion of the charcoal in the oxygen of the niter, fuses the barium sulphate with the sodium carbonate, and decomposes them into barium carbonate and sodium sulphate; thus,

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3$$

The fused mass is thrown into boiling water, which dissolves the sodium sulphate and leaves the barium carbonate. The latter may be allowed to settle, and is then washed several times by decantation with distilled water, until the washings no longer yield a precipitate with barium chloride, showing that the whole of the sodium sulphate has been washed away and pure barium carbonate remains.

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## STRONTIUM.

*Symbol Sr. Atomic weight 87.2. Valence II.*

**115. History and Occurrence.**—Strontium was distinguished as a peculiar substance by Hope, in 1792. Davy, in 1808, recognized it as an elementary body, though it was not until 1855 that Bunsen and Matthiessen obtained it in the pure state. Strontium occurs in nature both as sulphate and carbonate. The former, known as the mineral *celestine* or *celestite* (so called from the blue tint of many specimens*), is mostly found in beautiful crystals associated with the native sulphur in Sicily; the latter is found in the mineral *strontianite*—derived from Strontian, Scotland, where the mineral was first observed, and from which the metal obtained its name *strontium*.

* Said to be due to the presence of ferrosoferric phosphate.

**116. Preparation and Properties.**—Metallic strontium is usually prepared by the electrolysis of its chloride, though it has been obtained in quantity by distilling strontium amalgam in hydrogen. The amalgam was prepared by the action of sodium amalgam on a saturated solution of strontium chloride.

Strontium is a pale-yellow metal, of specific gravity 2.54; it is harder than lead, melting at red heat, and if exposed to air burning vividly with a characteristic crimson flame. Though it is quite permanent in dry air, it decomposes water readily, with the evolution of hydrogen.

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## COMPOUNDS OF STRONTIUM.

**117. Strontium Oxide.**—Strontium oxide, or ***strontia***, $SrO$, is, as a rule, obtained by igniting strontium nitrate $Sr(NO_3)_2$. It is a grayish-white, porous mass. It is infusible, and unites energetically with water to form the hydrate.

**118. Strontium Dioxide.**—Strontium dioxide, or peroxide, $SrO_2$, is precipitated, in combination with water, when a solution of strontium oxide in water is mixed with hydrogen peroxide.

**119. Strontium Hydroxide.**—Strontium hydroxide, or hydrate, $Sr(OH)_2$, is made on a large scale by heating the native strontium sulphate with brown iron ore (hydrated ferric oxide) and coal dust. On treating the product with water, ferrous sulphide remains undissolved, and $Sr(OH)_2$ passes into solution. It is used in sugar refining. It is less soluble than barium hydrate and is converted into strontium oxide by heat.

**120. Strontium Nitrate.**—Strontium nitrate $Sr(NO_3)_2$, the preparation of which is similar to that of barium nitrate, is deposited from its hot aqueous solution in anhydrous octahedrons, and crystallizes at low temperatures in oblique rhombic tablets containing 5 molecules of water of crystallization. Strontium nitrate is soluble in water, but insoluble

in alcohol. It is largely used in the manufacture of *red fire.*

**121. Strontium Chloride.**—Strontium chloride $SrCl_2$ crystallizes in needles having the composition $SrCl_2, 6Aq$. It differs from $BaCl_2$ in being deliquescent and fairly soluble in alcohol; the alcoholic solution burns with a red flame.

**122. Strontium Carbonate and Sulphate.**—The carbonate of strontium, strontianite $SrCO_3$, and strontium sulphate, celestine $SrSO_4$, are found in nature, as has been previously mentioned. These two salts are insoluble in water, and are deposited as white precipitates on adding a soluble carbonate or sulphate to the solution of a strontium salt. Strontium sulphate is, however, less insoluble than barium sulphate. Strontium salts impart a crimson tinge to an otherwise colorless flame.

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## CALCIUM.

*Symbol Ca. Atomic weight 39.9. Valence II.*

**123. History and Occurrence.**—Calcium carbonate and sulphate were known to the ancients, the former being burned into lime for making mortar. It is from the Latin word for lime, *calx*, that the name calcium has been derived. The metal itself was discovered by Davy in 1808 and isolated in 1854 by Matthiessen, who obtained it by decomposing fused calcium chloride by means of the voltaic current.

Like barium and strontium, calcium is found, though far more abundantly than either, in the mineral kingdom. As carbonate, it forms the mineral calcite and the rock masses known as *limestone*, *chalk*, and *marble*. As sulphate, it forms vast beds of *gypsum*; as phosphate, it occurs as *apatite*; as fluoride, in fluorspar, etc. Calcium, moreover, is found in all animals and vegetables, and its presence in their food, in one form or other, is an essential condition of their existence.

**124. Preparation and Properties.**—Metallic calcium may be obtained by decomposing fused calcium iodide with

metallic sodium, or by the electrolysis of its chloride, previously mixed with two-thirds of its weight of strontium chloride, and fused in a porcelain crucible. Metallic calcium has a light-yellow, brilliant color, is about as hard as gold, and very ductile and malleable. It oxidizes slowly in the air, though it is permanent in perfectly dry air. It decomposes water at ordinary temperatures. It is lighter than barium and strontium, its specific gravity being 1.57, and it is more easily fused. The salts of calcium impart a red tinge to an otherwise colorless flame.

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## COMPOUNDS OF CALCIUM.

**125. Calcium Oxide.**—Calcium oxide $CaO$, universally known as **lime,** is always prepared on a large scale by igni-

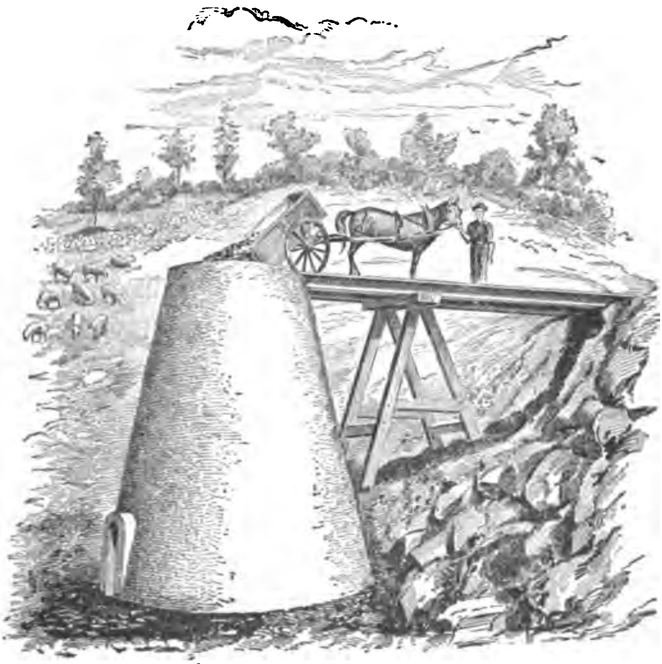

FIG. 5.

ting its carbonate. This operation is conducted in a rather

rude furnace of masonry, called a *kiln*. These kilns are usually located adjacent to the side of the hill containing the limestone quarry, as shown in Fig. 5, and a platform is built from the hill, over which the stone is hauled and dumped into the top of the kiln, in which an opening is left, not only for charging, but as an exit for the gases and smoke evolved during the process of burning.

The *charge*, as the quarried limestone is called when placed in the kiln, rests on an arch built on the hearth with large pieces of limestone. It is piled up nearly to the top of the kiln, as shown in Fig. 6. The fire is built on the hearth, and lighted near the back, so that it will become more intense towards the mouth as the draft increases.

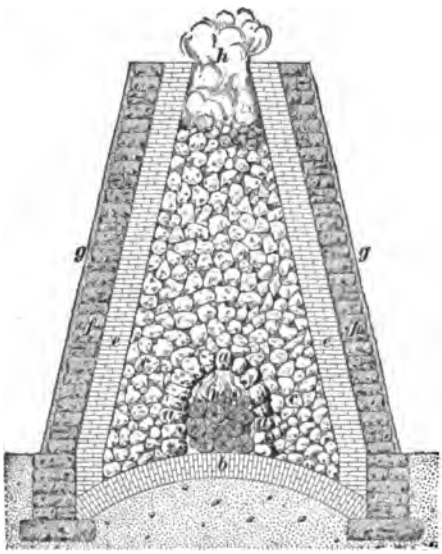

FIG. 6.

The air entering by the fire-door carries the flame to all parts of the arch, and gradually brings the limestone to a state of white heat. Fig. 6 shows the section of a conical lime kiln such as is usually built in this country; *a* shows the limestone arch that rests on the firebrick hearth *b*, and under which the fire is built; *c* is the loose limestone thrown around and over the arch *a*, and is composed of smaller pieces of rock. At *e* is shown the inside lining of the kiln, composed of fire-brick; *f* is the wall of the kiln itself, built of either stone or brick; *g* is the outside coating or plastering of clay, put on to keep as much of the heat in the kiln as possible; *h* shows the upper opening through which the kiln is charged, and also acting as a chimney for the escape of smoke, etc. At *j* is

shown the wood fire that produces the necessary heat required.

The usual test of the quality of the lime thus obtained consists in sprinkling it with water, with which it should eagerly combine, evolving much heat, swelling to about 2½ times its bulk and crumbling to a light white powder of calcium hydrate $Ca(OH)_2$.

Calcium oxide is a white, hard, infusible substance having a specific gravity of 2.3 to 3.

**126. Calcium Hydrate.**—Calcium hydrate, or hydroxide $Ca(OH)_2$, is obtained by slaking lime, that is, by adding water to $CaO$, as has been previously mentioned. It is a soft, white, bulky powder. It requires 530 times its weight of cold water to dissolve it, and nearly twice as much hot water, forming an alkaline, slightly caustic liquid known as *lime water*, which yields, on evaporation in vacuo, hexagonal prisms of the hydrate. Lime water readily absorbs $CO_2$ from the atmosphere, becoming milky, and precipitates $CaCO_3$. Calcium hydrate is easily converted into calcium oxide by heat. It is widely used in manufacturing chemistry, being the cheapest alkaline substance.

**127. Calcium Chloride.**—Calcium chloride $CaCl_2$ is produced by dissolving either calcium oxide or carbonate (chalk or white marble, for instance) in hydrochloric acid, and is frequently obtained as a waste product in the chemical arts, as in the manufacture of ammonia from ammonium chloride and quicklime:

$$2NH_4Cl + CaO = CaCl_2 + H_2O + 2NH_3$$

On evaporating a solution of calcium chloride in water, prismatic crystals of the composition $CaCl_2, 6Aq$ are obtained, which dissolve again in about one-fourth of their own weight of water. These crystals $(CaCl_2, 6Aq)$ lose 2 molecules of water when dried in vacuo, and the whole 6 molecules at 200°. The calcium chloride thus obtained, free from water, is used as a drying agent in the laboratory, as it possesses a great eagerness to combine with water. (See Art. **5** and

Experiment 5, *Inorganic Chemistry*, Part 1.) In consequence of the attraction of calcium chloride for water, surfaces wetted with a solution never get dry, and this solution is, consequently, frequently employed to make mantelets, for the protection of gunners, and also to render various objects, such as ropes, scenery, etc. in theaters, reasonably fireproof.

The crystals of calcium chloride are used with snow as a freezing mixture; in it a thermometer falls to $-48.5°$. Calcium chloride melts at a full red heat, and if heated in the air evolves chlorine. A saturated solution of calcium chloride boils at 180°, and is sometimes used in the laboratory as a convenient bath for obtaining a temperature above the boiling point of water.

**128. Calcium Carbide.**—Calcium carbide $CaC_2$ is obtained, according to Moissan, a French chemist, in the following way: At the high temperature of the electric furnace, lime is promptly reduced by carbon, but metallic calcium is not obtained. The reduced metal combines with part of the carbon, forming a black, homogeneous, crystalline mass, which is calcium carbide. It has a specific gravity of 2.2, and is only fusible at the high temperature at which it has been originally obtained. When heated in the air it burns into calcium carbonate $CaCO_3$. Water instantly reacts with it, forming calcium hydrate and acetylene, according to the equation:

$$\underset{\text{calcium carbide}}{CaC_2} + \underset{\text{water}}{2H_2O} = \underset{\text{calcium hydrate}}{Ca(OH)_2} + \underset{\text{acetylene}}{C_2H_2}$$

**129. Calcium Nitrate.**—This salt is formed in nature in the vicinity of dwellings, in the soils of cellars, in damp walls, and as an efflorescence on the walls of stables and other places through which urine or other organic liquids percolate, and is, consequently, frequently called *lime saltpeter*, or *wall saltpeter*. It may be prepared by saturating nitric acid with calcium carbonate.

Calcium nitrate has the formula $Ca(NO_3)_2.4Aq$, and differs from the corresponding salts of barium and strontium by

being deliquescent, much more soluble in water, and soluble in alcohol.

**130. Calcium Carbonate.**—Calcium carbonate $CaCO_3$, generally known as *carbonate of lime*, from which all the manufactured compounds of lime are derived, constitutes the different varieties of limestone met with in nature in such great abundance. It is dimorphous, being orthorhombic in *aragonite* and rhombohedral in *calcite*. Iceland spar (mentioned in Arts. **158,** *et seq.*, *Physics*) is calcite that is colorless and perfectly transparent, with crystals doubly refracting.

*Limestone* and *chalk* are simply calcium carbonate in an amorphous state, and are known to the agriculturist as *mild lime*. Marble, in its different varieties, is an assemblage of minute crystalline grains of calcium carbonate, sometimes variegated by the presence of oxides of iron and manganese, or of bituminous matter, the last constituent giving the color to what is known as black marble.

Calcium carbonate is a chief constituent of the shell of fishes and of egg shells; in fact, no mineral compound, except calcium phosphate, has so large a share in the composition of animal frames. Corals also consist chiefly of calcium carbonate derived from the skeletons of innumerable minute insects. The mineral *gaylussite* $CaCO_3, Na_2CO_3, 5Aq$ is a double carbonate of calcium and sodium, and is scarcely affected by water unless previously heated, when water dissolves out the sodium carbonate. *Baryta calcite* $BaCO_3, CaCO_3$ is a double carbonate of barium and calcium.

**131. Calcium Sulphate.**—Calcium sulphate $CaSO_4$, or *sulphate of lime*, is met in nature in combination with water as $CaSO_4, 2H_2O$ in two different forms. It occurs in the form of transparent prisms as *selenite*, and in opaque or semi-opaque masses known as *alabaster* and *gypsum*. It is the latter form that yields *plaster of Paris*, for, when heated to between 150° and 200°, it loses $\frac{3}{4}$ of its water, becoming $2CaSO_4, H_2O$; and, if the mass is then powdered and mixed

with water, the powder recombines with the water to form a mass, the hardness of which nearly equals that of the original gypsum.

In the preparation of plaster of Paris, a number of large lumps of gypsum are built up into a series of arches, upon which the rest of the gypsum is supported; under these arches the fuel is burned, and its flame is allowed to traverse the gypsum, care being taken that the temperature does not rise too high, or the gypsum is overburned and sets very slowly with water.

When the operation is supposed to be completed, the lumps are carefully sorted, and those that appear to have been properly calcined are ground to a fine powder. When this powder is mixed with sufficient water to form a creamy liquid and poured into a mold, the minute particles of calcium sulphate combine with water to reproduce the original gypsum $CaSO_4,2H_2O$, and in this act of combination a slight expansion occurs which forces the plaster into the finest line of the mold. The setting is due to the fact that a small portion of the plaster $2CaSO_4,H_2O$ dissolves in the water, crystallizing, however, again immediately as $CaSO_4,2H_2O$, thus leaving the water free to dissolve another portion of $2CaSO_4,H_2O$, which crystallizes in its turn as $CaSO_4,2H_2O$. In this way the mass soon becomes one of interlaced crystals of $CaSO_4,2H_2O$. An addition of about one-tenth of lime to the plaster not only helps to harden it, but also accelerates the setting.

*Stucco* consists of a mixture of plaster of Paris and glue; certain cements used for building purposes are prepared from burnt gypsum which has been soaked in a solution of alum and then again burned; and, although the material thus obtained takes a considerably longer time to set than the ordinary kind. it is much harder, and therefore takes a good polish.

Plaster of Paris is always more or less damaged by long exposure to moisture, owing to the fact that it regains from the moist air a portion of its water, and its property of setting is so far diminished.

Precipitated calcium sulphate is used in the manufacture

of paper, under the name of *pearl hardener*. Calcium sulphate is used in stables and farmyards for absorbing the ammonia of the decomposing animal excrements, which would otherwise be lost to the manure.

Calcium sulphate is contained in most natural waters, and is one of the chief causes of the permanent hardness which is not removed by boiling. It is much more soluble in water than is strontium sulphate, so that sulphates will precipitate calcium only from strong solutions. The aqueous solution of $CaSO_4$ precipitates barium salts immediately, but strontium salts only after an interval, on account of the greater solubility of $SrSO_4$. Calcium sulphate is most soluble in water having a temperature of 35°; 1 part of it then dissolves in 400 parts of water. It is insoluble in alcohol. Boiling $HCl$ dissolves it, and deposits it in needle-shaped crystals on cooling.

**132. Chloride of Lime.**—See Arts. **65** to **68**, inclusive, *Inorganic Chemistry*, Part 1.

**133. Calcium Fluoride.**—Calcium fluoride $CaF_2$, which has been previously mentioned as fluorspar, occurs in the bones and teeth. Many specimens of it decrepitate and emit a phosphorescent light when heated. It fuses at red heat, and is used in metallurgical operations as a flux, since it attacks silicate at a high temperature. Calcium fluoride is slightly soluble in hot $HCl$, and is precipitated by $NH_3$.

**134. Calcium Sulphide.**—Calcium sulphide $CaS$ may be obtained by reducing calcium sulphate at a high temperature with charcoal or hydrogen. It has obtained some importance on account of its presence in so called *luminous paints*. The discovery of its most remarkable property of shining in the dark dates back to 1761, when Canton first observed it; his so called "phosphorus" was obtained by strongly heating oyster shells with sulphur. The phosphorescence is not, however, due to slow oxidation, since a specimen which has been kept for over one hundred years in a sealed tube still exhibits this property.

When $CaO$ is acted on by $H_2S$, it yields a crystalline *calcium hydrosulphide* $Ca(SH)_2$. When this is heated in $H_2S$, it is decomposed; thus,

$$Ca(SH)_2 = CaS + H_2S$$

The $CaS$ is a white solid, soluble in water. When $Ca(SH)_2$ is exposed to air, it deliquesces, evolves $H_2S$, and becomes $Ca(SH)(OH)$:

$$Ca(SH)_2 + H_2O = H_2S + Ca(SH)(OH)$$

Calcium sulphide occurs, combined with $CaO$, in the tank waste of the alkali works. A solution of $Ca(SH)_2$ is used as a depilatory.

**135. Calcium Phosphate.**—Calcium phosphate $Ca_3(PO_4)_2$ is found in the minerals *apatite*, *phosphorite*, *sombrerite*, and *coprolite;* in the first two, it is met combined with calcium fluoride, forming $3Ca_3(PO_4)_2, CaF_2$, and this is also contained in bone ash, of which $Ca_3(PO_4)_2$ forms the larger proportion (approximately 80 per cent.). This is sold as a *non-mercurial plate powder*, under the trade name of *white rouge.*

Calcium phosphate is nearly insoluble in water, but it is dissolved by $HCl$ and $HNO_3$, and is precipitated again by ammonia. When $CaCl_2$ is added to $Na_2HPO_4$, a gelatinous precipitate is obtained, which becomes crystalline after a short time. The gelatinous precipitate dissolves readily in acetic acid $HC_2H_3O_2$, but the crystalline precipitate does not; and, if the solution of the gelatinous precipitate in a very little acetic acid is allowed to stand, it deposits crystals of $CaHPO_4, 2Aq$. This salt is found in the stone-like concretions, called *calculi*, in the bladder and kidneys of the sturgeon.

**136. Tetrahydrogen Calcium Phosphate.**—Tetrahydrogen calcium phosphate $H_4Ca(PO_4)_2$, more generally known as *superphosphate of lime*, is prepared by decomposing $Ca_3(PO_4)_2$ with $H_2SO_4$, according to the equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = H_4Ca(PO_4)_2 + 2CaSO_4$$

The calcium sulphate $CaSO_4$ thus obtained is filtered off, and the superphosphate of lime is left in solution. The chemically pure superphosphate of lime may be obtained by dissolving bone ash in $HCl$, precipitating the solution with ammonia, and digesting the washed precipitate of $Ca_3(PO_4)_2$ with $H_3PO_4$, according to the subjoined equation:

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2$$

On allowing the solution to evaporate spontaneously, the salt crystallizes in rhomboidal plates containing 1 molecule of water. It is dissolved by a small quantity of water, but is decomposed and precipitated by much water, or by boiling:

$$CaH_4(PO_4)_2 = H_3PO_4 + CaHPO_4$$

The commercial superphosphate of lime, known as *superphosphate manure*, prepared by decomposing ground mineral phosphates with sulphuric acid, is valued by the farmer for the large amount of soluble phosphate it contains. In course of time, the proportion of soluble phosphate is found to have decreased, and the phosphate is said to have *reverted* to the insoluble form; one reason assigned for this is the action of the superphosphate upon some undecomposed $Ca_3(PO_4)_2$ remaining in the compound, resulting in the formation of the insoluble hydrocalcium phosphate:

$$CaH_4(PO_4)_2 + Ca_3(PO_4)_2 = 4CaHPO_4$$

Another cause of this *retrogression* of the superphosphate, which has been prepared from mineral phosphates, is the presence of the sulphates of aluminum, magnesium, and iron, which gradually convert the phosphoric acid into insoluble forms.

**137. Calcium Pyrophosphate.**—Calcium pyrophosphate $Ca_2P_2O_7$ forms, when exposed to red heat, a perfectly transparent glass, which has a specific gravity of 2.6, and which can not only be worked into lenses and prisms, like ordinary glass, but also possesses the property of resisting the action of all acids, including hydrofluoric acid, at ordinary temperature.

**138. Calcium-Ammonium Arsenate.**—Calcium-ammonium arsenate $CaNH_4AsO_4,7Aq$ is obtained as a white precipitate by mixing $CaCl_2$ with excess of $NH_3$, and adding arsenic acid. The precipitate is gelatinous at first, but changes rapidly into fine needle-shaped crystals. It is slightly soluble in water, but almost insoluble in ammonia. Dried in vacuo over sulphuric acid, it becomes $Ca_3NH_4H_2(AsO_4)_3,3Aq$. Dried at 100°, it has the formula $Ca_6NH_4H_6(AsO_4)_6,3Aq$. Heated to redness, it becomes *calcium pyro-arsenate* $Ca_2As_2O_7$.

Calcium ortho-arsenate $Ca_3(AsO_4)_2$, as well as metarsenate $Ca(AsO_3)_2$, has also been obtained.

**139. Calcium Silicates.**—Calcium silicates are found, associated with silicates of other metals, in many minerals. They also enter into the composition of most glasses. Window glass, for instance, contains the silicates of calcium and sodium, and Bohemian glass those of calcium and potassium.

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## REVIEW OF THE METALS OF THE ALKALINE EARTHS.

**140.** Owing to their close relationship, *barium*, *strontium*, and *calcium* form a rather interesting natural group of metals. They exhibit a well defined gradation in their attraction for oxygen; namely, barium is more readily tarnished or oxidized, even in dry air, than strontium, and strontium, again, more readily than calcium. The hydroxides of the metals exhibit a similar gradation in properties; *barium hydroxide* does not lose water, however strongly it may be heated, whereas the *hydroxides of strontium and calcium* are readily decomposed by red heat. Barium hydroxide and strontium hydroxide are far more soluble in water than is calcium hydroxide, and all of these three exhibit a very decided alkaline reaction, which certainly entitles them to the name of *alkaline earths*.

Among the other compounds of these metals, the sulphates

may be mentioned as presenting a gradation of a similar description; for barium sulphate may be considered insoluble in water, while strontium sulphate is slightly soluble, and calcium sulphate rather freely soluble.

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## MAGNESIUM.

*Symbol Mg. Atomic weight 23.94. Valence II.*

**141. History and Occurrence.**—Magnesium carbonate, under the name of *magnesia alba*, has been known in Europe since the beginning of the eighteenth century, but, although Black in 1775 showed that this substance appeared to be a peculiar earth, its composition was not known until 1808, when Davy obtained the metal. The magnesium he obtained was rather impure; and not until 1830, and then by Bussy, was it produced in an approximately pure form. Bunsen and Matthiessen, in 1852, prepared it by electrolysis of fused magnesium chloride; and, in 1857, Deville and Caron obtained it in large quantities by acting upon the chloride with sodium, a process subsequently improved by Sonstadt.

Magnesium is found abundantly, like calcium, in all three natural kingdoms. Among minerals containing this metal, those with which we are most familiar are certain combinations of silica and magnesia, well known by the names of *talc*, *steatite*, or *French chalk*, *asbestos*, and *meerschaum;* nearly all minerals containing magnesium possess a peculiar soapy feeling. The magnesium compounds employed in medicine are derived either from the mineral *dolomite*, or *magnesium limestone*, which contains the carbonates of magnesium and calcium, or from the magnesium sulphate, which is obtained either from sea-water or from the waters of certain mineral springs.

**142. Preparation and Properties.**—Magnesium is prepared on a small scale by mixing 900 grams of magnesium chloride with 150 grams of calcium fluoride, 150 grams

of fused sodium chloride, and 150 grams of sodium cut in thin slices. The mixture is thrown into a red-hot earthen crucible, which is then covered and again heated. When the action appears to have terminated, the fused mass is stirred with an iron rod, to promote the union of the globules of magnesium. It is then poured upon an iron tray, allowed to solidify, broken up, and the globules of magnesium separated from the slag; they may be united into one globule by throwing them into a melted mixture of chlorides of magnesium and sodium and fluoride of calcium.

Magnesium is a silver-white, brilliant metal, having a specific gravity of 1.76. It is somewhat malleable and ductile, but is not very tenacious. It melts at a red heat, and may be obtained crystallized in regular octahedrons. At higher temperatures it is volatile. It oxidizes readily in moist air, but is not attacked by dry air. Acids attack it with ease, and it unites directly with most negative elements, including nitrogen.

Metallic magnesium has acquired considerable importance in the past few years as a source of light. It may be readily drawn into a wire or rolled into a ribbon. When the extremity of such a wire is heated in a flame, it takes fire, and burns with white light of great brilliancy,* becoming thereby converted into magnesia $MgO$. If the burning wire end is plunged into a jar filled with oxygen, the combustion is far more brilliant; the wire then burns with an incomparable splendor that the eye cannot endure; at the same time the jar becomes filled with a dense, white smoke which condenses into a white powder (magnesia).

The light emitted by burning magnesium is capable of inducing chemical changes similar to those caused by sunlight, a circumstance turned to advantage for the production of photographic pictures by night, in mines, etc., where, in the form of powder, magnesium is employed in the so called "flash light."

Numerous attempts and experiments have been made to

* A magnesium wire of .33 millimeter thickness emits a light of approximately 75 candlepower.

utilize magnesium for general illuminating purposes, but the large quantity of solid magnesia produced in its combustion appears to form the most serious obstacle to its extended use.

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### COMPOUNDS OF MAGNESIUM.

**143. Magnesium Oxide, or Magnesia.** — Magnesia $MgO$ occurs in nature as the mineral *periclasite* crystallized in isometric forms; it is the sole product of the combustion of magnesium in the air, and is left whenever its carbonate, hydrate, or nitrate is ignited. It forms a soft, bulky, insoluble white powder, which slowly attracts moisture and carbonic acid from the air, to form the hydrate $Mg(OH)_2$ and the carbonate $MgCO_3$.

**144. Magnesium Hydrate.**—Magnesium hydrate, or magnesium hydroxide $Mg(OH)_2$, occurs in nature crystallized as the mineral *brucite*. When $MgO$ is mixed with $H_2O$, combination takes place, but not with any considerable evolution of heat, as is the case with $BaO$, $SrO$, and $CaO$. If excess of water is carefully avoided, the mass sets like plaster of Paris. It is precipitated from solutions of magnesium salts by alkali hydrates, such as caustic potash. Magnesium hydrate slowly absorbs the carbon dioxide from the air, and is readily decomposed by heat into $MgO$ and $H_2O$. It is principally used in extracting sugar from the sugar beets.

**145. Magnesium Chloride.**—Magnesium chloride $MgCl_2$ is most readily prepared by igniting the double chloride of magnesium and ammonium, the ammonium chloride is thereby driven off and the magnesium chloride is left as a white, translucent, crystalline mass, readily fusible and somewhat volatile.

Magnesium chloride is very soluble in water, and rapidly attracts the moisture of the atmosphere. Like all soluble salts of magnesium, it has a decidedly bitter taste. When magnesia is moistened with a strong solution of magnesium

chloride, it sets into a hard mass resembling plaster of Paris. Magnesium chloride may be mixed with several times its weight of sand, and will bind the sand closely together.

*Carnallite* $KCl,MgCl_2,6Aq$ is found in crystals in the Stassfurt salt mines. It is decomposed by water into its constituent salts. *Bischofite* $MgCl_2,6Aq$ is found associated with carnallite.

**146. Magnesium Carbonate.**—Magnesium carbonate $MgCO_3$, known as the mineral *magnesite*, occurs in nature crystallized in rhombohedrons. *Magnesia alba*, the common commercial form of this substance, is obtained by precipitating the sulphate with sodium carbonate and boiling, it has the general composition $5MgCO_3,2Mg(OH)_2,7Aq$; the reaction which occurs may be expressed by the following equation:

$$7MgSO_4 + 7Na_2CO_3 + 2H_2O$$
$$= 5MgCO_3,2Mg(OH)_2 + 7Na_2SO_4 + 2CO_2$$

Magnesium carbonate, like calcium carbonate, is soluble in carbonic acid, and is present in most natural waters, causing temporary hardness, the $MgCO_3$ being precipitated by boiling.

When magnesia alba is dissolved in carbonic-acid water, and the solution exposed to air, needles of $MgCO_3,3Aq$ are deposited.

**Dolomite,** or **magnesian limestone,** is a mixture of magnesium carbonate and calcium carbonate in variable proportions. Magnesium carbonate is prepared from it by heating it sufficiently to decompose the $MgCO_3$ and exposing it, under pressure, to the action of water and carbon dioxide, when the $MgO$ is dissolved and the $CaCO_3$ is left. By passing steam through the solution, the basic magnesium carbonate is precipitated.

**147. Magnesium Sulphate.** — Magnesium sulphate $MgSO_4,H_2O,6Aq$ exists in solution in sea-water, and in certain purgative mineral waters, such as those of Epsom in England, whence the name *Epsom salt*, so frequently

applied to this substance. It is sometimes prepared by calcining dolomite (see Art. **146**) to expel the carbon dioxide, washing the residual mixture of lime and magnesia with water to remove part of the lime, and treating it with sulphuric acid, which converts the calcium and magnesium into sulphates; and, since calcium sulphate is difficultly soluble in water (see Table 8, *Theoretical Chemistry*), it is readily separated from the magnesium sulphate, which is easily soluble in water, according to the above quoted table, and is obtained by evaporation in prismatic crystals, having the previously mentioned composition $MgSO_4, H_2O, 6Aq$.

Epsom salt is now made from the mineral *kieserite* $MgSO_4, H_2O$, found abundantly in the Stassfurt salt mines. This is, apparently, almost insoluble in water, but, when kept for some time in continuous contact with water, it is slowly but surely converted into $MgSO_4, 7H_2O$.

In some parts of Spain, magnesium sulphate is found in large quantities as an efflorescence upon the soil, similar to niter in tropical climates. This sulphate, as well as that contained in well water, appears to have been produced by the action of the calcium sulphate, originally present in the water, upon magnesian limestone rocks, a reaction that may be represented by the subjoined equation:

$$MgCO_3 + CaSO_4 = MgSO_4 + CaCO_3$$

The crystals $MgSO_4, 7H_2O$ fuse easily, and become $MgSO_4, H_2O$ when subjected to a temperature of about 150°. The last molecule of water, however, can only be expelled at above 200°, and, from its intimate relationship to the compound, is termed its *water of constitution.*

The water of constitution in the magnesium sulphate may be displaced by the sulphate of an alkali metal without alteration in its crystalline form; a double sulphate of magnesium and potassium, $MgSO_4, K_2SO_4, 6Aq$, and a similar salt of ammonium may thus be obtained. A somewhat remarkable salt, having the composition $MgSO_4, K_2SO_4, 2CaSO_4, 2H_2O$, and known under the name of *polyhalite*, as well as *kainite*, having the composition $K_2SO_4, MgSO_4, MgCl_2, 6Aq$, both

found in the Stassfurt mines, may here be mentioned; the former is readily decomposed by water into its constituent salts.

Epsom salt dissolves very easily in water, but not in alcohol. If the aqueous solution is mixed with sufficient alcohol to render it turbid, small oily drops separate, from which small crystals presently shoot out, and the liquid becomes, by degrees, a pasty mass of very light needles closely interlaced, which contain $7H_2O$. An aqueous solution crystallized at above 70° deposits $MgSO_4,H_2O,5Aq$; at 0°, crystals of $MgSO_4,H_2O,11Aq$ are formed.

**148. Phosphates of Magnesium.**—$Mg_3(PO_4)_2$ is contained in the bones of animals and in some seeds. $MgHPO_4,7Aq$ is the precipitate produced by $Na_2HPO_4$ in magnesium salts; it is decomposed by boiling with water:

$$3MgHPO_4 = H_3PO_4 + Mg_3(PO_4)_2.$$

$MgNH_4PO_4,6Aq$ is deposited in crystals from alkaline urine, and forms *triple phosphate calculi.* It is precipitated by $Na_2HPO_4$ from a magnesium salt to which $NH_3$ has been added:

$$MgSO_4 + NH_3 + Na_2HPO_4 = Na_2SO_4 + MgNH_4PO_4$$

The precipitation is greatly accelerated by stirring. The $MgNH_4PO_4$ is nearly insoluble in water, and in ammonia.

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## ZINC.

*Symbol Zn. Atomic weight 64.9. Density 32.45. Valence II. Molecular weight 64.9. One liter of zinc vapor weighs 2.91 grams (32.45 criths).*

**149. History and Occurrence.**—Zinc occupies a high position among useful metals, being peculiarly fitted, on account of its lightness, etc., for the construction of pipes, roofs, etc. An ore of zinc was used by the ancient Greeks, under the name *cadmia*, in the manufacture of brass. The

first zinc was obtained in Europe in the eighteenth century, it having been, until that time, imported from China. The name *zinc* was given to the metal by Paracelsus in the sixteenth century.

The ores of zinc are found pretty abundantly in this country, in England (Somersetshire, Cumberland, Cornwall, and Derbyshire), Transylvania, Hungary, and Silesia.

Metallic zinc, as a rule, does not occur free in nature. It is claimed to have been found in the native state near Melbourne, in Australia. Its chief ores are *smithsonite*, or *zinc carbonate* $ZnCO_3$, *blende*, or *zinc sulphide* $ZnS$, *red zinc ore*, in which zinc oxide $ZnO$ is associated with the oxides of iron and manganese, and franklinite $ZnO, Fe_2O_3$.

Zinc carbonite is one of the most important ores of zinc. It is found largely in England, and a basic carbonate, $ZnCO_3, 2Zn(OH)_2$, occurs in Spain. Formerly the name *calamine* was given to both the carbonate and the silicate, but at present the carbonate is known as *smithsonite*, the hydrated silicate, $Zn_2SiO_4, H_2O$, as *calamine*, and the anhydrous silicate, $Zn_2SiO_4$, as *willemite*.

**Blende** has derived its name from the German word *blenden*, meaning "to dazzle," in allusion to the brilliancy of its crystals, which are generally almost black from the presence of iron sulphide, the true color of pure zinc sulphide, however, being white. Blende is found in North America, Germany, Bohemia, England, Wales, etc. It is generally associated with lead sulphide (galena), which must always be carefully picked out of the ore before smelting it, since it would become converted into lead oxide, which would corrode the earthen retorts employed in the zinc-reduction process.

**150. Preparation.**—Zinc is extracted from its ores by first roasting them in a reverberatory furnace, and then distilling them, mixed with charcoal, in close iron or earthen vessels. By the action of charcoal, the oxygen is removed from the zinc oxide which constitutes the roasted ore, and the zinc thus set free, being volatile, distils over into suitable receivers. The process, as a whole, varies in different

countries, and it is not within the scope of this section to go closely into the various ways of manufacturing zinc, as these are strictly metallurgical operations. Suffice to say that, in Silesia, Germany, this distillation is effected in peculiarly shaped muffles of fireclay, in Belgium in earthenware tubes, and in England in fireclay retorts. An English zinc furnace is shown in Fig. 7. It is conical in shape, and has an interior dome, within which six crucibles are placed, each of them having a hole in the bottom, through which an iron pipe passes to take away the zinc vapor. The crucibles are charged with the mixture of roasted zinc ore and coke, the covers are cemented on, and the crucibles are gradually raised to bright redness. At first the carbon monoxide burns at the mouth of the tube, but soon the greenish flame of zinc appears; the tube is then lengthened, and the condensed zinc is collected in suitable vessels placed beneath. It is afterwards remelted, cast into ingots, and sent out under the commercial name *spelter*. The spelter or zinc of commerce is impure, containing as a rule small quantities, or only traces—according to the constitution of the ore—of iron, copper, lead, cadmium, carbon, and arsenic. It may be purified to a certain degree by repeated meltings with small quantities of niter, but the last traces of impurity can be removed only by fractional distillation in vacuo.

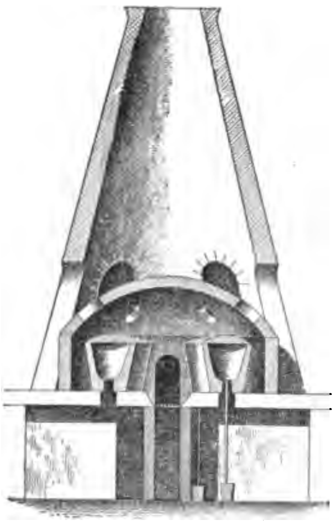

FIG. 7.

**151. Properties.**—Zinc is a bluish-white, highly crystalline metal; its specific gravity is about 7; its fracture is laminated and brilliant. Zinc is hard and brittle at ordinary temperatures, and also at 200°; but between 100° and 150°

it is malleable and ductile and may be rolled into thin sheets. At 412° it melts, and at 1040° it boils, evolving a vapor having half the normal density, from which the conclusion is drawn that its molecule is monatomic.

When heated to redness in air, zinc volatilizes and burns with a greenish flame into a smoke of oxide, which falls in light, white flakes, which were formerly known as *flowers of zinc*, or *philosopher's wool.*

Zinc dissolves with the evolution of hydrogen in hydrochloric and sulphuric acid, and in boiling solutions of potassium and sodium hydrates (see Experiments 3 and 4, *Inorganic Chemistry*, Part 1). When perfectly pure, zinc is dissolved with difficulty by dilute sulphuric acid at ordinary temperatures, and the easy solubility of the commercial metal must be attributed to the presence of small quantities of foreign metals. The latter being electronegative in contact with zinc, form voltaic couples, in which the zinc is the more oxidizable metal.

The great strength of iron has been ingeniously combined with the durability of zinc, in the so called *galvanized iron.* This is manufactured by coating clean iron sheets with melted zinc, thus affording a protection much needed in and around large towns, where the sulphurous and sulphuric acids arising from the combustion of coal, and the acid emanations from various factories, greatly accelerate the corrosion of unprotected iron.

The iron plates thus coated are at first thoroughly cleaned, similar to a process which will be more particularly treated on in the manufacture of tin plate, and are then dipped into a vessel of melted zinc, the surface of which is coated with sal ammoniac (ammonium chloride), in order to dissolve the zinc oxide which forms upon the surface of the metal and might adhere to the iron plate so as to prevent its becoming uniformly coated with the zinc.* A more firmly adhering

* The sal ammoniac acts on the heated zinc according to the equation $Zn + 2NH_4Cl = ZnCl_2 + 2NH_3 + H_2$, and the zinc chloride which is formed dissolves the oxide from the surface of the metal, producing zinc oxychloride.

coat of zinc is obtained by first depositing a thin film of tin upon the surface of the iron plate by galvanic action, whence the name *galvanized iron* is derived.

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## COMPOUNDS OF ZINC.

**152. Zinc Oxide.**—$ZnO$ is the only zinc oxide known; it occurs in nature as *red zinc ore*, or *zincite*. It is the sole product of the combustion of zinc in the air. It is commercially known as *zinc white*, or *Chinese white*, and is prepared by allowing the vapor of the metal to burn in earthen chambers through which a steady current of air is maintained. It is a white powder, unaltered in the air, becoming transiently yellow on heating, and is practically insoluble in water.

Zinc oxide is frequently used for painting, instead of *white lead*, over which it has the advantages of not injuring the health of the persons using it, and of being unaffected by hydrogen sulphide—an important consideration, especially in manufacturing towns, where that compound is continually and abundantly contaminating the atmosphere. Unfortunately, however, the zinc-oxide paint is much more liable to peel off than white-lead paint. Zinc oxide has a specific gravity of 5.6. It is sometimes used in the manufacture of glass for optical purposes.

**153. Zinc Hydrate.**—Zinc hydrate, or zinc hydroxide $Zn(OH)_2$, is obtained as a gelatinous precipitate when caustic alkalies are added to solutions containing zinc; thus,

$$ZnSO_4 + 2KOH = K_2SO_4 + Zn(OH)_2$$

The precipitate dissolves in the excess of alkali, and, if this is not too great, is reprecipitated by boiling. Zinc hydrate is readily decomposed by heat; thus,

$$Zn(OH)_2 = ZnO + H_2O$$

**154. Zinc Sulphide.**—Zinc sulphide $ZnS$ is found crystallized in nature, forming the mineral *sphalerite*, or *blende*. It

is generally yellowish brown in color, has a resinous luster, and is translucent.

It is precipitated from zinc solutions by alkali sulphides as a white precipitate, easily soluble in acids. The native sulphide is easily converted into the sulphate by roasting it with free access of air.

**155. Zinc Chloride.**—Zinc chloride $ZnCl_2$ is prepared in the laboratory by dissolving zinc in hydrochloric acid. The aqueous solution, evaporated to a syrupy consistency, deposits a hydrated chloride $ZnCl_2, H_2O$, crystallizing in deliquescent octahedrons. This salt loses its water when strongly heated, and melts at about 250°. On cooling, a solid white mass is obtained, which is the anhydrous chloride; in this state it is very void of water, and deliquesces when exposed to the air. It volatilizes without decomposition at a red heat. It is very soluble in water, and dissolves also in alcohol.

**156. Zinc Sulphate.**—Zinc sulphate $ZnSO_4, H_2O, 6Aq$, known as *white vitriol*, bears a dangerous resemblance to Epsom salt, but it loses its water of crystallization at 100°, and is decomposed at a very high temperature into $ZnO$, sulphur dioxide, and oxygen, whereas $MgSO_4$ bears fusion without being decomposed. Hence, $ZnSO_4$, when heated to redness, leaves a residue that is yellow when hot and white when cold.

At temperatures above 40° zinc sulphate crystallizes as $ZnSO_4, H_2O, 5Aq$, which is isomorphous with the corresponding salt of magnesium. Like magnesium sulphate, it forms double sulphates, in which the $H_2O$ is replaced by alkali sulphates—$ZnSO_4, K_2SO_4, 6Aq$ and $ZnSO_4, (NH_4)_2SO_4, 6Aq$ are isomorphous with the $Mg$ double salts. Like all true isomorphous salts, the sulphates of magnesium and zinc crystallize together from their mixed solutions.

Zinc sulphate is prepared on a large scale by roasting blende at a low red heat, when it combines with $O$ from the air to form $ZnSO_4$, which is dissolved out by water and crystallized. It has a metallic, nauseous taste, and is frequently used in pharmacy, as well as for dyeing purposes.

## CADMIUM.

*Symbol Cd. Atomic weight 111.6. Density 55.8. Valence II. Molecular weight 111.6.*

**157. History and Preparation.**—Cadmium was discovered in 1817 by Hermann, and also by Strohmeyer, the latter giving to it the name *cadmium*, from *cadmia*, the ancient name of *zinc ore*. This metal is generally found associated with zinc, either as oxide in calamine or as sulphide in zinc blende. It occurs as an impurity in commercial zinc, but, as it is more volatile than zinc, it comes over in the first products of its distillation; these are dissolved in acid, and the cadmium precipitated by zinc, in the metallic state.

**158. Properties.**—Cadmium resembles zinc, its compounds being analogous to those of this metal, but it is whiter, heavier, and more easily volatile and fusible than this metal. It is ductile and malleable at ordinary temperatures, but becomes brittle at about 82°, and if bent when in this condition it crackles like tin. It has a specific gravity of about 8.7, melts at 315°, and crystallizes in regular octahedrons on cooling. It is not attacked by air, but acids act on it slowly. At a red heat it burns, producing brown fumes of oxide.

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## COMPOUNDS OF CADMIUM.

**159. Cadmium Oxide.**—Cadmium oxide $CdO$ may be obtained by calcining either cadmium carbonate or nitrate. Its color varies from yellowish brown to dark brown. It is reduced at high temperatures by carbon and by hydrogen, its reduction taking place more readily than that of zinc oxide.

**160. Cadmium Sulphide.**—Cadmium sulphide $CdS$ occurs native as *greenockite* in the form of bright-yellow, hexagonal prisms, terminated by six-sided pyramids.

It is prepared in the laboratory by precipitating a solution of cadmium salt with hydrogen sulphide or a soluble sulphide, an amorphous precipitate of a fine yellow color being thus obtained.

**161. Cadmium Iodide.**—Cadmium iodide $CdI_2$ is obtained by digesting finely divided cadmium with iodine in the presence of water. It crystallizes from its aqueous solution in transparent, hexagonal prisms having a brilliant luster. It is soluble in water and alcohol. Cadmium iodide, as well as cadmium brómide $CdBr_2,4Aq$, is used in photography.

**162. Cadmium Sulphate.**—Cadmium sulphate $3CdSO_4,8H_2O$ is obtained by dissolving either the metal, its oxide, or its carbonate in dilute sulphuric acid.

**163. Cadmium Chloride.**—Cadmium chloride $CdCl_2,2Aq$ effloresces in air, while zinc chloride deliquesces. Moreover, it may be dried without partial decomposition. It is fusible and volatile like zinc chloride.

**164.** Cadmium differs from all other metals in forming a yellow sulphide insoluble in alkalies, so that its salts, mixed with excess of ammonia and treated with $H_2S$, give a yellow precipitate.

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## BERYLLIUM.

*Symbol Be. Atomic weight 9. Valence II.*

**165.** This rather rare metal, which is also known as *glucinum Gl*, is found associated with silica and alumina in the green precious stone *emerald*, which is a double silicate of $AlO_3$ and $BeO$ having the formula $Al_2O_3,3BeO,6SiO_2$, and appears to owe its color to the presence of a minute quantity of chromium oxide. The more common mineral *beryl*, or *aquamarine*, has a similar composition, but is of a paler green color, which is apparently caused by the presence of iron.

Metallic beryllium is obtained by passing the vapor of the chloride over melted sodium. It is a white and brilliant metal, having a specific gravity of 2.1, and melts at a temperature below that of silver. It may be forged and rolled into sheets like gold. It does not decompose water, even by the aid of heat, and it is readily attacked by hydrochloric and sulphuric acids, with the evolution of hydrogen.

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## COMPOUNDS OF BERYLLIUM.

**166. Beryllium Chloride.**—Beryllium chloride $BeCl_2$ is generally prepared by passing chlorine over an intimate mixture of beryllium oxide and charcoal at high temperature.

Beryllium chloride forms white, deliquescent crystals which fume in the air. It is fusible, and volatilizes at a red heat. It is very soluble in water, and forms a hydrate that is decomposed by heat, yielding beryllium oxide and hydrochloric acid.

**167. Beryllium Oxide.**—Beryllium oxide $BeO$ is prepared from beryl or by precipitating a solution of beryllium chloride with ammonia. In the latter case, a hydrate $Be(OH)_2$ is obtained, which is converted into oxide by heat.

Beryllium oxide is a light, white, infusible powder, soluble in acids and alkalies. When heated in the oxyhydrogen flame, it volatilizes like magnesium and zinc oxides.

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## REVIEW OF THE MAGNESIUM GROUP OF METALS.

**168.** This group includes the metals *Be*, *Mg*, *Zn*, *Cd*, and *Hg*. As in the case of the preceding groups of metals, the melting point falls with the rise of atomic weight ($Hg = 200$; melts at $-39°$), while the specific gravity rises with the atomic weight. Their order of chemical energy, on the other hand, is the reverse of that of the metals of the preceding group, falling with the rise of the atomic weight. Their oxides are practically insoluble in water, and are less

basic as the molecular weight increases. The carbonates are easily decomposed by heat; the sulphates are more easily decomposed than those of the metals of the preceding groups, and appear to decrease in stability with the rise of molecular weight. The vapors of these metals contain monatomic molecules.

Mercury *Hg* will be considered later.

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## ALUMINUM.

*Symbol Al. Atomic weight 27.3. Valence III* (?).

**169. History and Occurrence.**—Aluminum is distinguished among metals, as silicon is among non-metallic bodies, for its great abundance in the solid mineral portion of the earth. *Alumina*, or *aluminum oxide*, was long confounded with lime, from which it was first distinguished by Marggraff, in 1754. Oersted, in 1826, first prepared the chloride, and from this, in 1828, Wöhler obtained the metal. This process was made a commercial one by St. Claire Deville in 1854. The metal was first prepared from cryolite by H. Rose in 1855. The minerals corundum, ruby, and sapphire are aluminum oxides; diaspore, chrysoberyl, and spinel are aluminates; micas, feldspar, and clays are aluminum silicates; cryolite is sodium aluminum fluoride; and many other minerals contain it as an essential constituent.

Its name is derived from the Latin *alumen*, alum being a substance largely imported into Europe from the East until the fifteenth century.

**170. Preparation.**—Aluminum is mostly produced commercially by the process invented by St. Claire Deville, and which consists in reducing the chloride with sodium. At the works of Morin in Paris, France, 10 parts of sodium aluminum chloride, 5 parts of cryolite or fluorspar, and 2 parts of sodium are mixed together and thrown upon the hearth of a reverberatory furnace, previously heated to full redness. A violent action takes place, great heat is evolved,

and the liquefied mass of slag and metal gathers at the back of the furnace. The latter is drawn off and cast into ingots. This process has been, however, lately much improved by Castner. Tissier, at Amfreville, France, makes aluminum from the mineral cryolite, after a method proposed by H. Rose; and in the United States it is now produced in considerable quantities from the same mineral by electrolysis, a process devised by Hall.

**171. Properties.**—Aluminum is a white metal with a somewhat bluish luster when polished. It crystallizes in octahedrons, and is a good conductor of heat and electricity. It is ductile, malleable, highly sonorous, and very light, its specific gravity being 2.56 to 2.67. It is less fusible than tin and zinc, but more so than silver, its fusing point being 625°.* It requires a very high temperature to vaporize it. Like zinc, it is most easily rolled and bent between 100° and 150°.

Aluminum is unaltered by the air, even by moist air. When heated in thin sheets in a current of oxygen, it burns and is converted into aluminum oxide. Nitric and sulphuric acids scarcely attack it. Hydrochloric acid dissolves it readily, disengaging hydrogen; it is also immediately attacked by boiling solutions of potassium or sodium hydrates, the hydrogen being disengaged and alkaline aluminates formed.

**172. Uses of Aluminum.**—The remarkable lightness of this metal renders it extremely useful in the manufacture of beams of chemical balances, and of small weights, such as the decigram, centigram, and milligram, since these weights when made of aluminum are more than three times larger than those of brass, and nearly nine times larger than when made of platinum; besides, the relative indestructibility of aluminum by the fumes of acids makes these weights still more valuable. The metal has also been lately used in the manufacture of cooking utensils, and especially of canteen

* It is not easily fused before the blowpipe, as its surface becomes covered with infusible oxide.

vessels for military purposes, where this metal, on account of its lightness and ability to resist vegetable acids, has proved itself extremely useful. Aluminum is also employed in the manufacture of writing pens, and for ornamental purposes, for, though it does not obtain quite as bright a polish as silver, it has the advantage of not being blackened by hydrogen sulphide, which so readily discolors silver. The chief impurities of the commercial aluminum are traces of iron and silicon.

When aluminum is fused with nine times its weight of copper, it forms an alloy, known as *aluminum bronze*, which is not only very similar to gold in appearance, but is also nearly as strong as iron. Its use for ornamental purposes has been somewhat retarded by the fact that this bronze does not retain its brilliancy as completely as gold.

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## COMPOUNDS OF ALUMINUM.

**173. Aluminum Oxide.**—Aluminum oxide $Al_2O_3$, generally known as *alumina*, occurs native in the mineral *corundum*, which includes the precious stones known as the *ruby* and the *sapphire*, as well as the valuable polishing material called *emery*, distinguished by its extreme hardness, in which it ranks next to the diamond.

It may be prepared by the combustion of the metal in oxygen or by igniting the hydrate.

**174. Aluminum Hydrate.**—Aluminum hydrate $Al(OH)_3$ is found crystallized as *hydrargillite* or *gibbsite.*

The artificially prepared aluminum hydrate is characterized by its gelatinous appearance. If a little alum is dissolved in warm water, and some ammonia added to the solution, the alumina will precipitate as a semitransparent gelatinous mass of the hydrate, having the formula $Al(OH)_3, 2H_2O$. It is nearly insoluble in ammonia, but readily dissolves in potash as well as in soda solutions. Aluminum hydrate may be obtained in solution in water by dissolving it in a solution

of $AlCl_3$ and dialyzing. It resembles a solution of silicic acid in that it is very easily gelatinized. When washed and dried, the gelatinous hydrate shrinks very much, and forms a mass resembling gum. Aluminum hydrate has a great attraction for most coloring matters, with which it forms insoluble compounds known as *lakes;* thus, for instance, if alum is mixed with an infusion of logwood, and a little ammonia added, the aluminum hydrate will form, together with the coloring matter, a purplish-red lake, which may be filtered off, leaving the solution colorless. This property is turned to advantage in calico printing, where the compounds of alumina are largely used as *mordants.*

**175. Aluminum Chloride.**—Aluminum chloride $AlCl_3$, also sometimes written as $Al_2Cl_6$, is prepared by passing over an incandescent mixture of alumina and charcoal a current of chlorine, aluminum chloride and carbon monoxide being formed according to the equation:

$$Al_2O_3 + 3C + 3Cl_2 = 3CO + 2AlCl_3$$

The aluminum chloride thus obtained is a white, semicrystalline, waxy substance, having sometimes a light-yellow color; it is fusible, and volatilizes in the air at a temperature slightly above 100°. When exposed to the air, aluminum chloride gives off white fumes and readily attracts moisture. It dissolves in water with the production of heat.

A solution of aluminum chloride may be obtained by dissolving gelatinous alumina in hydrochloric acid. When this solution is evaporated, it decomposes as soon as it attains a certain degree of concentration, disengaging hydrochloric acid and leaving aluminum oxide.

Aluminum chloride readily combines with sodium chloride, forming a double chloride $AlCl_3, NaCl$.

**176. Aluminum Sulphate.**—Aluminum sulphate $Al_2(SO_4)_3, 18H_2O$ is obtained in the arts by decomposing non-ferruginous (free from iron) clays with sulphuric acid. It crystallizes with difficulty in needles and in thin pearly scales, in which state it contains 18 molecules of water of

crystallization. It dissolves in 2 parts of cold water. When slowly heated, it first loses its water of crystallization until at a higher temperature it gives off sulphuric anhydride $SO_3$, leaving a residue of alumina, according to the equation:

$$Al_2(SO_4)_3 = 3SO_3 + Al_2O_3$$

It is seen that aluminum sulphate represents 3 molecules of sulphuric acid, in which the 6 atoms of hydrogen have been replaced by the sexivalent couple $Al_2$; thus,

$$\left.\begin{matrix} H_2SO_4 \\ H_2SO_4 \\ H_2SO_4 \end{matrix}\right\} + Al_2O_3 = 3H_2O + (Al_2)^{vi} \left\{\begin{matrix} SO_4 \\ SO_4 \\ SO_4 \end{matrix}\right.$$

**177. Aluminum and Potassium Double Sulphate.** Aluminum and potassium double sulphate, more generally known as **alum** $Al_2(SO_4)_3, K_2SO_4, 24H_2O$, is obtained as a crystalline deposit by adding to a concentrated solution of potassium sulphate a concentrated solution of aluminum sulphate, and stirring the mixture well with a glass rod.

Alum is only sparingly soluble in cold water, but dissolves more easily in hot, and quite abundantly in boiling water, being deposited from the latter, on cooling, in voluminous, transparent octahedrons. When heated, these crystals melt in their own water of crystallization (24 molecules), and in losing this water the melted mass swells up considerably.

Alum may also be obtained crystallized in cubes, and it is prepared in this form near Civita Vecchia, Italy, by working a mineral that contains the elements of alum with a large excess of alumina. This mineral is known as *aluminite*, and the cubical alum is known as *Roman alum*.

This cubical variety may be prepared in the laboratory by adding a small quantity of potassium carbonate to a hot solution of ordinary alum, so that the precipitate first formed will be redissolved on agitating the liquid. On cooling, cubical, opaque crystals are deposited. These are formed under the influence of a small quantity of basic sulphate (aluminum sulphate combined with an excess of alumina) contained in the liquid, and which probably enters

into the constitution of the crystals. With this slight difference, octahedral and cubical alum represents the same composition, which is expressed by the formula

$$Al_2(SO_4)_3, K_2SO_4, 24H_2O, \text{ or } AlK(SO_4)_2, 12H_2O$$

**178. Other Alums.**—Ammonium alum is obtained by adding ammonium sulphate to a solution of aluminum sulphate. It possesses a composition analogous to that of ordinary alum, with which it is isomorphous. It contains:

$$Al_2(SO_4)_3, (NH_4)_2SO_4, 24H_2O$$

It is very often substituted in the arts for potassium alum, being cheaper than the latter. When strongly calcined, it leaves a residue of pure alumina.

Other alums are known, in which iron, manganese, and chromium play the part taken by aluminum in ordinary alum. These alums are all isomorphous. By the action of sulphuric acid on the sesquioxides of the above metals, sulphates are formed analogous to aluminum sulphate, and of which the composition is expressed by the general formula $(X_2)^{vi}(SO_4)_3$. With the sulphates $M_2SO_4$ they form alums, all of which crystallize in regular octahedrons, and which can be mixed in one and the same crystal without the form of the latter being affected by the mixture.

The following are the most important of these compounds:

| | |
|---|---|
| Manganese alum | $Mn_2(SO_4)_3, K_2SO_4, 24H_2O$ |
| Iron alum | $Fe_2(SO_4)_3, K_2SO_4, 24H_2O$ |
| Chromium alum | $Cr_2(SO_4)_3, K_2SO_4, 24H_2O$ |

It is seen that each of these presents an atomic composition similar to that of ordinary alum.

**179. Mineral Silicates of Aluminum.**—Many of the chemical formulas of minerals that contain silicates of alumina, associated with the silicates of other metallic oxides, are complicated, from the circumstance that a part of the aluminum is very often replaced by iron, which, in the form of sesquioxide $Fe_2O_3$, is isomorphous with it, and

therefore capable of replacing it without altering the crystalline form and general character of the mineral.

In a similar manner, the other metals present in a mineral may be exchanged for isomorphous representatives; thus, there are two well known feldspars: potash feldspar (orthoclase) and soda feldspar (albite), having the formulas

$$K_2O, Al_2O_3, 6SiO_2 \text{ and } Na_2O, Al_2O_3, 6SiO_2$$

respectively. These minerals are sometimes mingled in one and the same crystal, without bearing any definite equivalent proportion to each other; the formula of such a mineral would be written, for instance $(KNa)_2O, Al_2O_3, 6SiO_2$ (potash albite, or pericline).

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## GALLIUM.

*Symbol G (or Ga, according to some authorities). Atomic weight 69.8. Valence II and III.*

**180. History, Occurrence, and Preparation.**—The element gallium was discovered in 1875 by Lecoq de Boisbaudran in a zinc blende from the mine of Pierrefitte in the valley of Argeles, Pyrenees, in France. Its name is derived from Gallia, the Latin name of France. It is also found in the zinc ores of a few mines in Westphalia, Germany, and other places.

In order to extract the gallium from its ore, the ore is roasted and treated with sufficient $H_2SO_4$ to dissolve nearly all the zinc sulphide. The residue, containing the gallium, is dissolved in $H_2SO_4$, and the solution partly precipitated with sodium carbonate. The precipitate, containing all the gallium and part of the zinc, is dissolved in sulphuric acid, largely diluted, and boiled, to precipitate the titanic acid. The solution is mixed with acid ammonium acetate, and treated with hydrosulphuric acid. The precipitate, containing zinc and gallium, is dissolved in sulphuric acid, and again partially precipitated with sodium carbonate, which gives a deposit rich in gallium; this is dissolved in exactly the required quantity of sulphuric acid, diluted and boiled, when

basic gallium sulphate is deposited; on dissolving this in potash and decomposing the solution by the galvanic current, the gallium is deposited on the cathode.

**181. Properties.**—Gallium is a hard, white metal of specific gravity 5.9, and possesses a metallic luster recalling that of nickel. It is remarkable for its low fusing point (30°), which really means that it melts with the heat of the hand. It will remain liquid when cooled far below this temperature, but solidifies when touched with a piece of the solid metal. It is not oxidized by dry air until heated nearly to redness, and the oxidation is then only superficial. Nitric acid scarcely acts upon gallium in the cold, but dissolves it on heating. Hydrochloric acid and potash dissolve gallium with the evolution of heat.

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## COMPOUNDS OF GALLIUM.

**182.** *Gallium sesquioxide* $G_2O_3$, left on igniting the nitrate, is white. When heated in hydrogen, a part sublimes, and the rest is converted into a bluish-gray substance, which appears to be *gallium oxide* $GO$. Two *chlorides of gallium*, $GCl_2$ and $GCl_3$, exist; they are very fusible, volatile, and deliquescent. $GCl_2$ is oxidized to $GCl_3$ by potassium permanganate solution.

*Gallium sulphate* $G_2(SO_4)_3$ is very soluble in water; the solution deposits a basic salt when boiled. It combines with ammonium sulphate to form an alum, the solution of which is also precipitated by boiling.

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## INDIUM.

*Symbol In. Atomic weight 113.4. Valence II and III.*

**183. History, Preparation, and Properties.**—Indium is the name of a metal that was discovered in a specimen of zinc blende from Freiberg, Saxony, by Reich and Richter in 1863. They observed that the impure zinc chloride, obtained

by dissolving the roasted ore in hydrochloric acid, contained a substance whose spectrum consisted of two indigo-blue lines, one of which was very brilliant and more refrangible than the other. To extract indium from the Freiberg zinc, the metal is boiled with dilute sulphuric acid, employed in such quantities as to leave part of the zinc undissolved together with indium and lead. The residue is dissolved in nitric acid, the lead and cadmium precipitated by hydrosulphuric acid, the latter expelled by boiling, and the oxide of indium precipitated from the solution by barium carbonate. When this precipitate is dissolved in hydrochloric acid, and excess of ammonia added, the white indium hydroxide is precipitated, and may be reduced by heating in hydrogen. It is a white, malleable metal, resembling lead, and dissolves readily in hydrochloric and sulphuric acids. Its specific gravity is 7.2. Its fusing point is 176°, and it burns with a violet light, producing the oxide. It is, at ordinary temperatures, unaltered in the air, and produces a gray streak on paper.

## COMPOUNDS OF INDIUM.

**184.** *Indium oxide* $InO$ is a straw-yellow powder, becoming brown on heating, and easily reducible on charcoal. *Indium hydrate* $In''(OH)_2$ is thrown down, as a white precipitate, from solutions of indium by alkali hydrate. *Indium sulphide* $InS$ is a dark-yellow powder. *Indium chloride* $InCl_2$ is procurable as a white crystalline sublimate, which is deliquescent. *Indium sulphate* $In_2(SO_4)_3$ is easily obtained by dissolving the metal in sulphuric acid.

## REVIEW OF THE ALUMINUM GROUP OF METALS.

**185.** This group comprises *Al*, *G* (*Ga*), *In*, and *Tl* (thallium = 203.6). The last named metal bears the same relation to the other metals of the group as mercury bears to the other metals of the magnesium group (see Art. **168**). The melting points of the metals of the *Al* group do not descend

with the rise of the atomic weight; it is true that *Al*, which has the lowest atomic weight, has the highest melting point, but the remaining metals show a rise of melting point for increase of atomic weight (*Tl* melts at 290°). The specific gravity rises with the atomic weight (*Tl* has a specific gravity 11.9). As the atomic weight increases, there is a tendency for the formation of stable oxides lower than that typical of the group $R_2O_3$, and this typical oxide becomes less stable; this will be evident when the properties of thallium have been considered—a matter best postponed until *lead* has been studied.

The metals in the odd series of this group (see Table 2) are the rare elements *scandium*, *yttrium*, *lanthanum*, and *ytterbium*.

**186. Scandium.**—Scandium *Sc*, atomic weight 44.04, is the metal existing in the basic oxide *scandia* $Sc_2O_3$, which is found in the mineral *gadolinite*, and which consists of a mixture of silicates occurring at Ytterby in Sweden. The oxide is infusible and insoluble in alkalies. The metal has not been isolated, but the atomic weight is deduced from the equivalent of the oxide.

**187. Yttrium.**—Yttrium *Yt*, atomic weight 89.6, is the metal of the oxide yttria $Y_2O_3$, which is extracted from *gadolinite* and a similar mineral *samarskite*. Its exact properties are not well known. Yttria is a white oxide, and yttrium a gray powder.

**188. Lanthanum.**—Lanthanum *La*, atomic weight 139, also occurs in *gadolinite*, but is more abundant in *cerite*, a mineral of the same type also containing the metal *cerium*. The mixture of *lanthana* $La_2O_3$ and *ceria* obtained from this mineral is converted into nitrates which are fractionally crystallized, when the lanthanum nitrate separates first. When this is ignited it is converted into oxide which may be dissolved in *HCl*, and the chloride thus prepared may be fused with potassium to yield the metal lanthanum.

It is a white, malleable metal of specific gravity 6.16; it decomposes hot water, and oxidizes rapidly in air.

**189. Ytterbium.**—Ytterbium *Yb*, atomic weight 172.6, is only known as its oxide $Yb_2O_3$ at present.

**190.** Besides the above oxides, several others have been described as obtainable from the gadolinite minerals, e. g., *terbia*, *erbia*, *holmia*, *thulia*, *samaria*, *didymia*, etc. These *rare earths* have received much attention from the spectroscopist, to whom the evidence of their existence is solely due, and who is gradually arriving at the conclusion that they are of more complex composition than was at first supposed.

For a detailed account of these rare earths, which so far have found no practical applications in the arts, the student is referred to a more exhaustive treatise than this.

# INORGANIC CHEMISTRY.

(PART 4.)

## CHEMISTRY OF THE METALS.

### IRON.

*Symbol Fe. Atomic weight 55.9. Valence II, III*(?), *IV*(?), *and VI.*

**1. History and Occurrence.**—Iron is one of the most useful metals and at the same time one of those most widely and abundantly diffused in nature. It has been known from the earliest historic times—Tubal Cain being an artificer in this metal. It is doubtful whether it occurs native; the native iron found on the earth's surface generally contains nickel, and is of meteoric origin.

The chief forms of combination in which iron is found, in sufficient abundance to render them available as sources of the metal, are shown in Table 1.

These ores are frequently associated with extraneous minerals, some of the constituents of which are productive of injury to the quality of the iron. It is worthy of notice that scarcely one of the ores of iron is entirely free from sulphur and phosphorus—substances that have not only a serious effect on the quality of the iron extracted from those ores,

but also, by their presence in the iron, increase the difficulty of obtaining the metal in a marketable condition.

Iron occurs also in plants and vegetables, and is an essential constituent of the animal body.

TABLE 1.

| Common Name. | Chemical Name. | Combination. |
|---|---|---|
| Magnetic iron ore | Ferrosoferric oxide | $Fe_3O_4$ |
| Red hematite<br>Specular iron | Ferric oxide | $Fe_2O_3$ |
| Brown hematite, or limonite | Hydrated ferric oxide | $2Fe_2O_3, 3H_2O$ |
| Spathic iron ore | Ferrous carbonate | $FeCO_3$ |
| Clay ironstone ore | Ferrous carbonate with clay | |
| Blackband | Ferrous carbonate with clay and bituminous matter | |
| Iron pyrites | Bisulphide of iron | $FeS_2$ |

**2. Preparation and Properties.**—In the arts, iron is obtained on a large scale, either from the native oxide or from the artificial oxide obtained by roasting the native carbonate or hydrate.

Alternate layers of the ore, fuel, and limestone are placed in what is known as a *blast furnace*, which is from 40 to 100 feet high, and has its interior shaped like a double cone. A powerful blast of hot air enters at the bottom, and the combustible matter, at the high temperature thus produced, removes the oxygen from the ore, reducing it to the metallic state, according to the subjoined equation:

$$Fe_2O_3 + 3C = Fe_2 + 3CO$$

The limestone unites with the silica and other impurities present, forming an easily fusible silicate, which collects

above the melted iron and is drawn off as *slag*. After the iron is reduced to the metallic state, it takes up more carbon, becomes fusible, melts, and runs down to the bottom of the furnace, accumulating in a narrow cylinder, called the *crucible*, or *hearth*. When this is full, it is tapped by driving in the clay plug that closes the opening, and the melted iron runs down a suitable channel into molds made in the sand for its reception. The manufacture of cast iron in the blast furnace is a continuous operation; the materials are constantly added above, and the slag and melted iron are drawn off from below about six times a day, this being kept up usually until the furnace needs repairs, or until other reasons put a temporary stop to further manufacturing. The frequency with which the iron as well as the slag is drawn off varies in different places and under different conditions. It depends largely on the rapidity with which the iron is being produced. The iron thus obtained is known in the market as *cast*, or *pig*, *iron*.

*Varieties of Iron.*—Three varieties of this iron are known; namely, *white pig iron*, which is hard, brittle, and crystalline, uniformly brilliant and white, of specific gravity 7.5, and readily fusible; *gray pig iron*, which is granular in structure, of a gray color, very soft, difficultly fusible, and of specific gravity 7.1; and *mottled pig iron*, which has intermediate properties, but is stronger than either variety.

The *gray iron* has, as a rule, the least combined carbon, its color being due to a separation of a part of this carbon as graphite during the cooling. Hence, the same metal suddenly cooled, as when *chilled* or cast in iron molds, may be hard and white; and when cooled slowly in sand, be soft and gray. White iron, and especially an alloy of iron and manganese known as *spiegeleisen*, contains a relatively high percentage of carbon; gray iron contains considerably less.

Iron is refined, or converted into *wrought iron*, by burning out the carbon and silicon, as well as the impurities sulphur and phosphorus. This is effected usually by the process of *puddling*, or *boiling*. The pig iron is piled up on the floor of a reverberatory furnace, in contact with some of

the pure ores. On lighting the fire it melts, and is then continually stirred to mix it thoroughly with the oxide. The carbon and silicon are gradually oxidized, the former escaping as gaseous monoxide, and the latter being retained as silicate of iron in the slag, until finally the iron becomes pasty and clings together in spongy masses. These are collected into balls of about 30 kilograms weight, and compacted, first, by working between powerful jaws, called *squeezers*, and then between rolls, by which the slag is pressed out, and the iron is made into *muck bars*. The puddled bar is cut into short pieces, made into bundles, heated, and again passed through the rolls; this operation is repeated until the wrought iron is sufficiently pure. By this process the carbon is reduced to one-half of one per cent., sometimes to even less, and the other foreign matters to mere traces. If the iron retains phosphorus, it is brittle when cold, and is called *cold short;* if it retains sulphur, it is brittle when hot, or *red short*. The iron thus obtained is bluish gray in color, is fibrous in structure, and has a specific gravity of 7.3 to 7.9.

Pure iron may be prepared from the best commercial varieties, pianoforte wire, for instance, by fusing them with pure iron oxide, beneath a layer of glass to keep out the air, in a clay crucible. It is brilliant silver-white in color, softer than wrought iron, capable of receiving a high polish, strongly magnetic, of specific gravity 7.8, and crystallizes in the regular system. Iron is also prepared for pharmaceutical purposes by reducing its oxide by hydrogen at a red heat. It is then obtained as a black powder, which burns when heated in the air. In its purest commercial form, iron has a greater tenacity than any other metal, except nickel and cobalt. Its ductility is also very great, and when heated it may be rolled into sheets scarcely thicker than paper. At a full red heat it becomes pasty like wax, and may then be welded. It melts at a high temperature, probably above 2,000°.

*Manufacture of Steel.*—Steel, according to the American usage of the term, is iron that has been treated by one of a

variety of processes. The products included under this name contain from less than .1 to more than 1.5 per cent. of carbon and possess nearly all the chemical and physical properties, except those peculiar to cast iron, which belong to the commercial forms of this metal. A number of methods are in general use for making steel. In one, the wrought-iron bar is heated with charcoal, and thus made to again take up a portion of carbon; this is known as the *process of cementation.* Fig. 1 represents a cross-section of the furnace in which this is effected. The iron bars are

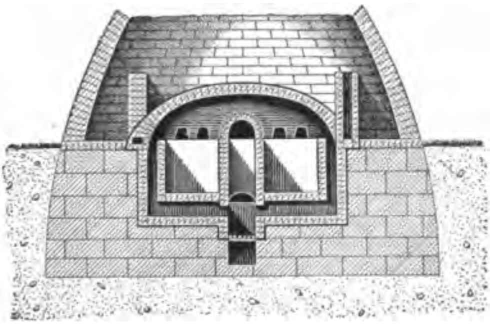

FIG. 1.

packed in charcoal in the fireclay chests, or boxes, shown in the figure, the whole covered with sand to exclude the air, and heated to redness for from seven to ten days, after which it is allowed to cool down slowly. The bars are now brittle, covered with blisters, and are easily fusible. They may be at once piled together, heated, and rolled into bars of *shear steel*, or they may be broken in small pieces, melted in crucibles of fireclay, with the addition of a little manganese dioxide, and cast into ingots; these ingots are afterwards drawn out under the hammer into bars. In this form it is known as *cast steel.*

Another process is known as the *Bessemer process*, a name derived from its inventor, Henry Bessemer. In the Bessemer process the molten pig iron is run into a *converter*, which is a large vessel of the shape shown in Fig. 2. It is made of iron plates and is lined with ganister (a fairly pure

sand). At the bottom of the vessel there are a number of openings of about ¼ inch in diameter, through which air is blown at a pressure of about 25 pounds per square inch. The charge (from 5 to 18 tons), having been melted in a separate furnace, is run into the converter, which is suspended on trunnions, so that it may be turned in a horizontal position for this purpose, and then replaced in a vertical position. The converter is previously heated by a little burning coke; it is then turned in a horizontal position, the molten iron is charged in, and the blast is turned on as it is rotated to a vertical position. The silicon and manganese burn first in the stream of air, producing a very high temperature; then the carbon is converted into carbon monoxide, which burns with a long flame at the mouth of the converter, and a little of the iron is burned to oxide, which forms a slag with the silica, and is carried up as a froth to the surface of the liquid iron. The blast of air, or *blow*, is continued until the disappearance of the flame of $CO$ indicates the completion of the process; the remainder of the purified iron is not pasty, as in the puddling furnace, but is retained in a perfectly liquid condition by the high temperature resulting from the combustion of the silicon, manganese, and carbon, so that the metal may be run out into ingot molds by tilting the converter. Formerly, attempts were made to stop the air blast at the right point, but the steel thus made varied so widely in quality that the process above described was substituted. Since the Bessemer process does not remove sulphur and phosphorus, it is evident that a cast iron as free from these impurities as possible must be employed. By simply lining the converter with a mixture of clay, silica, lime, and magnesia, constituting a basic material, Thomas and Gilchrist, in 1880, adapted the Bessemer process to the working of iron containing a notable amount of phosphorus.

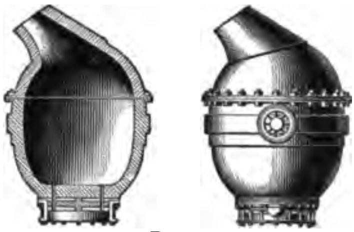

FIG. 2.

In the **Siemens-Martin,** or **open-hearth,** process, largely employed in this country, the pig iron is melted in a saucer-shaped depression made of iron plates lined with ganister. This hearth is built in a furnace so constructed that a flame of producer gas raised to a very high temperature by the system of regenerative firing, plays across the hearth. When the pigs have been thoroughly melted, scraps of iron plate, which, since they are of no other value, may be used to dilute the impure iron, are stirred in, and these are followed by an appropriate quantity of iron oxide, generally hematite. The oxidation of the impurities of the iron is effected in part by the oxygen of the hematite and in part by the excess of oxygen in the flame used to heat the hearth, the temperature of which is about 1,500°. When the aspect of a test piece withdrawn and hammered by the furnaceman indicates that the process is complete, the tapping hole of the furnace is unstopped, the metal run into a ladle and from there into ingots.

In this process the silicon is removed, chiefly in the form of iron silicate, as slag, which floats on the surface of the metal. It is customary to bring up the carbon contents of the metal in the ladle by the addition of a small quantity of *ferromanganese*, which immediately melts and mixes with the charge. Ferromanganese is an alloy of iron and manganese, which contains a relatively high percentage of carbon.

Malleable cast iron is produced by heating articles made of ordinary white cast iron to redness for several hours, in contact with an iron oxide. A reverse of the cementation process takes place, by which the carbon is partially removed and the iron becomes semimalleable.

**3. Properties of Steel.**—As steel is a term applied to a variety of material produced by various processes, and differing in chemical composition, its properties cannot be definitely stated, but differ with the different varieties. Ordinary steel, which contains a low percentage of carbon, is relatively soft and malleable, and probably cannot be hardened by any physical treatment. On the other hand, steel that contains more carbon, if heated to a rather high temperature

and suddenly cooled, or "quenched," by dipping it in cold water, becomes very hard. A steel containing a high percentage of carbon becomes much harder when treated in this way than one containing a smaller quantity of this element, and those samples containing but mere traces of carbon, as previously stated, cannot be hardened to any considerable extent by this process. It thus appears that the property of hardening when suddenly cooled from a high temperature depends largely, if not entirely, on the carbon content of the steel.

Careful study and examination of steel under varying conditions have led to the belief that the phenomena attending the hardening and softening of steel by changes of temperature, are due to the forms assumed by the carbon under varying conditions.

Osmond holds that there are two allotropic forms of iron, which he calls $\alpha$ and $\beta$ iron, and that the changes produced by changes in temperature are due to changes from one to the other of these forms. This theory, however, is not required to account for the changes observed, and is not generally accepted.

If a piece of high-carbon steel is heated to a high temperature and quenched, it becomes exceedingly hard—too hard, in fact, for ordinary purposes. If this is again heated to the same temperature and cooled slowly, it loses its hardness, and assumes the properties it possessed before heating; but if, instead of heating to the high temperature used in hardening, it is heated to a much lower temperature and cooled, suddenly as a rule, though not always, its hardness is modified or *tempered*, but not destroyed. It should be noted that the word *tempering* is frequently, and not altogether incorrectly, applied to any heating and sudden cooling of iron.

When the hardened steel is reheated, a thin film of oxide is formed on its surface, imparting different colors to the metal, by which its temperature may be judged with tolerable accuracy. In Table 2, which is compiled from the most reliable sources, the temperature to which steel is heated in tempering it for various instruments is given, together with the color assumed in each case.

TABLE 2.

TEMPERING OF STEEL.

| Temperature C. | Color. | Implements Thus Tempered. |
|---|---|---|
| 220°–232° | Straw-yellow. | Razors, lancets. |
| 243° | Yellow. | Penknives. |
| 254° | Brown-yellow. | Large shears for cutting metal. |
| 265° | Brown-purple. | Clasp knives. |
| 271° | Purple. | Table knives. |
| 276°–299° | Blue. | Watch springs, sword blades. |

**4.** Manganese, nickel, chromium, and tungsten, respectively, appear in steel to make it hard in whatever manner it is cooled, and are, therefore, used for making especially hard steel. Manganese steel, containing 12 per cent. of that metal, is said to be non-magnetic until it has been heated for some hours at 500–600°, when it becomes magnetic; if it is then heated above 800°, and quickly cooled, it again loses this property. Steel containing 25 per cent. of nickel is almost entirely non-magnetic when heated above 500°, and cooled slowly or rapidly, but becomes magnetic when cooled below 0°. It has been already stated that $P$ and $S$ make steel cold-short and red-short, respectively.

## OXIDES OF IRON.

**5.** Three oxides of iron are known, namely:

| | |
|---|---|
| Ferrous oxide | $FeO$ |
| Ferric oxide | $Fe_2O_3$ |
| Ferrosoferric oxide | $Fe_3O_4$ |

**6. Ferrous Oxide.**—Ferrous oxide $FeO$ may be obtained, by igniting ferrous oxalate in a closed vessel, as a black powder. *Ferrous hydroxide*, or *ferrous hydrate*, $Fe(OH)_2$, is formed as a greenish-white precipitate when an alkaline

hydrate is added to a solution of a ferrous salt, which is protected from the action of air. White flocks are thus produced, which, dried away from the air, have a slightly greenish tint, but which, on exposure, take fire and burn to ferric oxide. Ferrous oxide has a strong reducing action.

**7. Ferric Oxide.**—Ferric oxide $Fe_2O_3$ occurs abundantly in nature in two forms: one crystallized in rhombohedrons and mirror-like, called *specular iron;* the other columnar, or fibrous, sometimes amorphous in structure and blood-red in color, whence it is called *hematite.* Artificially it may be prepared by calcining ferrous sulphate, or green vitriol. This salt first loses its water, and then at red heat decomposes into sulphuric oxide, sulphurous oxide, and ferric oxide:

$$2FeSO_4 = SO_3 + SO_2 + Fe_2O_3$$

A red powder is thus obtained, which is known in commerce under the name of *colcothar*, *jeweler's rouge*, and *Venetian red*, and which is used for polishing metals, glass, etc. Its specific gravity is about 5. It is reduced to the metallic state when heated in hydrogen.

**8. Ferric Hydrates.** — Ferric hydrate $Fe(OH)_3$ or $Fe_2(OH)_6$ is precipitated as a reddish-brown compound when an alkaline hydrate is added to a ferric solution. If this is heated, water is expelled and a compound having the composition $Fe_2O(OH)_4$ is formed. Iron rust is generally considered as a hydrated oxide $2Fe_2O_3,3H_2O$, but some authors regard it as a mixture of oxide and hydrate $Fe_2O_3,Fe_2(OH)_6$.

Moist ferric hydrate forms the best antidote in cases of arsenical poisoning. It is used also in calico printing as a mordant, and in purifying gas.

**9. Ferrosoferric Oxide.** — This oxide of iron occurs native as *magnetic* or *black oxide of iron*, or *magnetite* $Fe_3O_4$. It is generally regarded as a compound of ferrous oxide with ferric oxide $Fe''O,Fe_2'''O_3$, a view confirmed by the occurrence of a number of minerals having the same crystalline

form as the native magnetic oxide of iron, in which the iron, or part of it, is displaced by other metals. Thus, *spinel* is $MgO,Al_2O_3$; *franklinite*, $ZnO,Fe_2O_3$; *chrome-iron ore*, $FeO,Cr_2O_3$; *pleonaste*, $MgO,Fe_2O_3$; *gahnite*, $ZnO,Al_2O_3$. The natural magnetic oxide was mentioned in Table 1 among the ores of iron. The *hydrated magnetic oxide of iron* $Fe_3O_4,H_2O$ is obtained as a black crystalline powder by mixing 1 molecule of ferrous sulphate with 1 molecule of ferric sulphate, and pouring the mixture into a slight excess of solution of ammonia, which is afterwards boiled with it. Magnetic oxide of iron, when acted on by acids, yields mixtures of ferrous and ferric salts, so that it is not an independent basic oxide.

The very stable character of $Fe_3O_4$ has permitted its application for protecting iron from rust. When superheated steam is passed over the red-hot metal, a very dense, strongly adhering film of $Fe_3O_4$ is produced, which effectually protects the metal (*Barff's process*). A similar coating is produced by the action of a mixture of air and carbon dioxide (*Bower's process*).

**10. Ferric Acid.**—Ferric acid $H_2FeO_4$ has not been obtained in the free state, but some of its salts are known.

When iron filings are strongly heated with niter, and the cooled mass treated with a little ice water, a fine purple solution of potassium ferrate is obtained. A better method of preparing this salt consists in suspending 1 part of freshly precipitated ferric hydrate in 50 parts of water, adding 30 parts of solid potassium hydrate, and passing chlorine till a slight effervescence commences:

$$Fe_2O_3 + 3Cl_2 + 10KOH = 6KCl + 2K_2FeO_4 + 5H_2O$$

The ferrate forms a black precipitate, and is insoluble in the strongly alkaline solution, though it dissolves in pure water to form a purple solution, which is decomposed even by dilution, oxygen escaping, and hydrated ferric oxide being precipitated. A similar decomposition takes place on boiling a strong solution, or on adding an acid with a view to

liberate the ferric acid. The ferrates of barium, strontium, and calcium are obtained as fine red precipitates when solutions of their salts are mixed with potassium ferrate.

As a lecture experiment, the ferrate may be prepared by precipitating the iron from a ferric-chloride solution with an excess of strong potassium-hydrate solution, adding a few drops of bromine, and heating. On dissolving the cold mass in water, a fine red solution is obtained, which gives a red precipitate with $BaCl_2$.

**11. Ferrous Carbonate.**—Ferrous carbonate $FeCO_3$ occurs in nature as *siderite*, or *spathic iron ore*, in obtuse rhombohedrons, light grayish white in color, and of specific gravity 3.8. It is thrown down, on the addition of a soluble carbonate to a solution of a ferrous salt, as a white precipitate, rapidly passing into brown ferric hydrate on drying. It is soluble in water containing carbonic acid and is found in this state in nature in the waters of chalybeate springs (see Art. **27**, *Inorganic Chemistry*, Part 1).

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## SULPHIDES OF IRON.

**12. Iron Disulphide.**—This sulphide of iron $Fe^{iv}S_2$, being a widely diffused mineral, is the most important of the sulphides of iron. It occurs native in two distinct forms: one, brass-yellow and isometric, is known as *pyrite;* and the other, white or dull greenish yellow and orthorhombic, is called *marcasite*. This latter variety can be altered much more readily than the other, and possesses a great tendency to attract oxygen from the air and become converted into *sulphate*. When heated in closed vessels, pyrites lose a part of their sulphur.

Ferric disulphide may be obtained artificially by heating iron with excess of sulphur to a temperature below redness, or by heating ferric oxide or hydrate moderately in a stream of $H_2S$ as long as it increases in weight.

Some kinds of pyrites explode with considerable violence

when heated, and create much alarm when they occur in household coal; these have been found to contain small cavities filled with highly compressed (probably liquid) $CO_2$, which expands suddenly when heated.

**13. Ferrous Sulphide.**—Ferrous sulphide $FeS$ is found in small quantities in many meteorites. It may be produced by the direct union of iron and sulphur, as when iron wire burns in sulphur vapor, or when the two substances are melted together in suitable proportions. It is a dark-gray solid with a metallic luster and crystalline structure, and is easily fusible. When finely divided, it is oxidized to ferrous sulphate on exposure to the air. With acids it evolves hydrogen-sulphide gas. It is precipitated in the form of a black sulphide, when an alkaline sulphide is added to an iron solution.

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## CHLORIDES OF IRON.

**14. Ferric Chloride.**—Ferric chloride $FeCl_3$ or $Fe_2Cl_6$ has been found in nature in crevices in active volcanoes. It is formed when a current of chlorine is passed over iron filings heated in a glass, or, better, a porcelain tube. The two elements unite with incandescence, and, if the chlorine is in excess, ferric chloride will be obtained as a brilliant, black, crystalline sublimate. The vapor of ferric chloride above 700° corresponds to $FeCl_3$, but at lower temperatures its composition is probably $Fe_2Cl_6$. Ferric chloride is deliquescent and dissolves in water with a hissing noise, forming a hydrated chloride. This hydrated chloride is also produced by dissolving iron in hydrochloric acid, heating the solution, and adding nitric acid so long as nitrous gas is evolved. On evaporation, orange-red rhombic crystals are deposited having the composition $FeCl_3, 3H_2O$.

**15. Ferrous Chloride.**—When hydrogen-chloride gas is passed over iron filings in excess, heated to redness, ferrous chloride $FeCl_2$ is obtained in white, shining, hexagonal

scales, which have a specific gravity of 2.5 and are deliquescent in moist air. Ferrous chloride is soluble in two parts of water, and the solution, evaporated and cooled away from the air, deposits bluish-green, monoclinic crystals, having the composition $FeCl_2, 4Aq$. Ferrous, like ferric, chloride forms double salts with alkali chlorides.

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## FERROUS SULPHATE.

**16.** Ferrous sulphate $FeSO_4$ has long been known under the names of *copperas*, *green vitriol*, and *sulphate of iron*. It is easily prepared by heating 1 part of iron wire with 1½ parts of strong sulphuric acid, mixed with four times its weight of water, until the whole of the metal is dissolved, when the solution is allowed to crystallize. It is produced on a large scale by exposing ferrous sulphide—obtained by roasting ferric disulphide, or pyrite—to the weather, by which it is oxidized:

$$FeS + 2O_2 = Fe''SO_4$$

It forms fine, green, rhomboidal crystals, having the composition $FeSO_4, H_2O, 6Aq$.

The color of the crystals varies somewhat, owing to the occasional presence of small quantities of ferric sulphate $Fe_2(SO_4)_3$. It dissolves very easily in twice its weight of cold water, yielding a pale-green solution. One part of boiling water dissolves about 2.5 parts of the crystals. When the commercial sulphate of iron is boiled with water, it yields a brown, muddy solution, in consequence of the decomposition of the ferric sulphate contained in it, with the precipitation of a basic sulphate. Ferrous sulphate has a great tendency to absorb oxygen and to become converted into ferric sulphate.

This disposition to absorb oxygen renders the ferrous sulphate useful as a reducing agent; thus, it is employed for precipitating gold in the metallic state from its solutions, but its chief use in the arts is for dyeing, for tanning, and for making writing ink.

## FERRIC SULPHATE.

**17.** Ferric sulphate $Fe_2(SO_4)_3$ is obtained by heating ferrous sulphate with nitric and sulphuric acids; the brown solution is evaporated, and the residue well dried:

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$$

Ferric sulphate is a slightly yellowish mass, which dissolves completely, though rather slowly, in water. The solution is yellow-brown, and has an acid reaction.

When concentrated by evaporation, it deposits a deliquescent, yellowish, crystalline mass, which constitutes hydrated ferric sulphate.

There are several *ferric subsulphates:*

$$H_2SO_4 + Fe_2O_3 = H_2O + \underset{\text{ferric monosulphate}}{(Fe_2O_2)''SO_4}$$

$$\left.\begin{matrix} H_2SO_4 \\ H_2SO_4 \end{matrix}\right\} + Fe_2O_3 = 2H_2O + \underset{\text{ferric disulphate}}{(Fe_2O)^{iv}\left\{\begin{matrix} SO_4 \\ SO_4 \end{matrix}\right.}$$

$$\left.\begin{matrix} H_2SO_4 \\ H_2SO_4 \\ H_2SO_4 \end{matrix}\right\} + Fe_2O_3 = 3H_2O + \underset{\text{normal ferric sulphate (ferric trisulphate)}}{(Fe_2)^{iv}\left\{\begin{matrix} SO_4 \\ SO_4 \\ SO_4 \end{matrix}\right.}$$

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## COBALT.

*Symbol Co. Atomic weight 58.6. Valence II and IV.*

**18. History and Occurrence.**—The property of coloring glass blue, possessed by certain cobalt compounds, was known to the ancient Romans and Greeks. Its ores were long known to the German miners under the name of *cobalt*, a name that has been derived from *kobold*, the evil spirit of the mines, who, as they supposed, tantalizingly offered them an ore rich in appearance, but worthless otherwise.

The metal was first prepared by Brandt in 1733, and thoroughly investigated by Bergmann in 1780. It is generally

found in combination with arsenic and sulphur, forming *tin-white cobalt* $CoAs_2$ and *cobalt glance* $CoAs_2, CoS_2$, but its ores also, as a rule, contain nickel, copper, iron, manganese, and bismuth.

**19. Preparation and Properties.**—Cobalt is obtained by strongly heating cobalt oxide with charcoal, in the manner to be described for preparing nickel from its oxide.

Cobalt has a steel-gray color, with a tinge of red; it is hard, has a granular fracture, a specific gravity of 8.7 to 8.9, and is malleable at a red heat. It takes up carbon and becomes fusible in an ordinary furnace. It is magnetic. When massive, its surface becomes tarnished on exposure to moist air. It oxidizes readily at a red heat, and burns in oxygen. Sulphuric and hydrochloric acids dissolve it slowly, with the evolution of hydrogen. Nitric acid acts on it readily.

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## COMPOUNDS OF COBALT.

**20.** Three oxides of cobalt, corresponding with those of iron, are known: *cobaltous oxide* $CoO$, *cobaltic oxide* $Co_2O_3$, and *cobalto-cobaltic oxide* $Co_3O_4$ or $CoO, Co_2O_3$.

**21. Cobaltous Oxide.**—Cobaltous oxide $CoO$ is a brown powder left when $Co(OH)_2$ is ignited in the absence of air; it is a basic oxide, dissolving in acids to form cobaltous salts. When heated in air, it oxidizes to $CoO, Co_2O_3$. When heated in the electric furnace, it melts and forms rose-colored crystals.

**22. Cobaltic Oxide.**—Cobaltic oxide $Co_2O_3$ is left as a black powder when cobaltous nitrate is gently heated. It is a feeble base, but the cobaltic salts are very unstable; thus, the oxide dissolves in cold $HCl$, yielding a brown solution of *cobaltic chloride* $Co_2Cl_6$, which is easily decomposed when subjected to heat, evolving $Cl_2$ and leaving $2CoCl_2$. When $Co_2O_3$ is heated, it becomes $CoO, Co_2O_3$.

**23. Cobalto-Cobaltic Oxide.**—Cobalto-cobaltic oxide $Co_3O_4$ or $CoO, Co_2O_3$ is the commercial oxide of cobalt

employed for painting on porcelain, and for preparing other commercial cobalt products. It is a black powder, which evolves chlorine when boiled with $HCl$, yielding a solution of $CoCl_2$. It is generally prepared as a bye product in the manufacture of nickel from its arsenical ores (see "Nickel"). $Co_3O_4$ is not an independent base, but gives cobaltous and cobaltic salts when dissolved in acids.

**24. Cobaltous Hydroxide.** — Cobaltous hydroxide $Co(OH)_2$ is obtained by adding potash in excess to a solution of a cobaltous salt, and boiling. The blue precipitate produced at first is a basic salt that becomes converted into the red hydroxide on boiling with excess of potash. If air is allowed access, it oxidizes the red precipitate, converting it into brown cobaltic hydroxide. $Co(OH)_2$ dissolves in ammonia, giving a fine red solution, which absorbs oxygen from the air and becomes brown. *Cobaltic hydroxide* $Co_2(OH)_6$ is a black compound, formed when the solution of a hypochlorite or hypobromite is added to a cobaltous salt.

**25. Cobaltous Nitrate.**—Cobaltous nitrate $Co(NO_3)_2, 6Aq$, obtained by dissolving cobaltous oxide in $HNO_3$ and crystallizing, forms red prisms, which become blue when their water is expelled, and black $Co_2O_3$ on further heating.

**Potassium-cobaltic nitrite** $K_6Co_2'''(NO_2)_{12}$, also known as *cobalt yellow*, is obtained as a yellow precipitate when cobaltous nitrate is acidified with acetic acid, and potassium nitrite added; the acetic acid liberates nitrous acid, which oxidizes the cobaltous salt:

$$2Co''(NO_3)_2 + 10KNO_2 + 4HNO_2$$
$$= K_6Co_2'''(NO_2)_{12} + 4KNO_3 + 2NO + 2H_2O$$

It forms a yellow, crystalline precipitate, which is slightly soluble in water, and not decomposable by either cold $HCl$ or $HNO_3$. Caustic alkalies decompose it, separating $Co_2(OH)_6$.

**26. Cobaltous Chloride.**—Cobaltous chloride $CoCl_2$ is obtained, by dissolving any of the oxides of cobalt in hydrochloric acid, as red prisms having the composition $CoCl_2, 6Aq$.

On being heated to 120°, these crystals lose 4 molecules of their water of crystallization, become blue, and have the composition $CoCl_2,2Aq$; if heated to 140°, they lose the remaining 2 molecules of water, and may be sublimed in dark-blue scales in a current of chlorine gas. If strong hydrochloric acid is added to a red solution of cobaltous chloride, it becomes blue; if enough water is now added to just give the solution a pink tinge, the blue color may be produced at pleasure by boiling, the solution first passing through a neutral tint.* Chloride of cobalt is frequently used as a so called *sympathetic ink*, for characters written with its pink solution are almost invisible until they are exposed to heat, that is, held before the fire, when the characters written with this ink become blue; they resume, however, their original pink color if exposed afterwards to the air.

**27. Sulphides of Cobalt.**—The *cobaltous sulphide* $CoS$ is obtained as a black precipitate when an alkaline sulphide is added to a solution of a salt of cobalt. It differs from $FeS$ by being only slightly soluble in $HCl$. A *cobaltic sulphide* $Co_2S_3$ is found in gray octahedrons, forming *cobalt pyrites*. The *disulphide* $CoS_2$ has been obtained artificially.

**28. Cobaltous Sulphate.**—Cobaltous sulphate $CoSO_4,7H_2O$ is found as *cobalt vitriol*. It forms red prisms isomorphous with ferrous sulphate. It does not acquire a blue color when dried, and can be submitted to a high temperature without undergoing decomposition. Cobaltic sulphate and cobaltic alums have been prepared.

**29. Cobaltous arsenate** $Co_3(AsO_4)_2,8Aq$, also known as *cobalt bloom*, is found in pink needles. *Cobalt diarsenide* $CoAs_2$ is found crystallized as *tin-white cobalt* and *speiss cobalt*, in which it is associated with the isomorphous arsenides of nickel and iron, so that it is usually written $(CoNiFe)As_2$. $CoAs_3$ is also found native.

* A solution containing so small a quantity as .015 per cent. of cobalt will give a distinct blue color when boiled with an equal volume of strong hydrochloric acid.

**30.** The **cobaltous silicate** associated with *potassium silicate* forms the blue color known as *smalt*, which is prepared by roasting the cobalt ore, so as to convert the bulk of the cobalt into oxide, leaving, however, a considerable quantity of arsenic as well as sulphur in the ore. The residue is then fused in a crucible with a mixture of ground quartz and carbonate of potash, when a blue glass is formed, containing cobalt silicate and potassium silicate; while the iron, nickel, and copper, combined with arsenic and sulphur, collect at the bottom of the crucible and form a fused mass of metallic appearance known as *speiss*, which is employed as a source of nickel. The blue glass is poured into cold water, so that it may be more easily reduced to the fine powder in which the smalt is sold. If the cobalt ore destined for smalt is overroasted, so as to convert the iron into oxide, this will pass into the smalt as a silicate, injuring its color. Smalt has a great resemblance to ultramarine, but is not bleached by acids.

**Zaffer** is prepared by roasting a mixture of cobalt ore with two or three parts of sand.

**Thenard's blue,** or **cobalt ultramarine,** consists of cobalt phosphate and aluminum phosphate, and is prepared by mixing precipitated alumina with cobalt phosphate, and calcining in a covered crucible. The phosphate is prepared by precipitating a solution of cobalt nitrate with phosphate of potassium or sodium.

**Rinmann's green** is prepared by calcining the precipitate produced by sodium carbonate in a mixture of cobalt sulphate, with zinc sulphate. It is a compound of the oxides of cobalt and zinc.

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## NICKEL.

*Symbol Ni. Atomic weight 58.6. Valence II, III, and IV.*

**31. History and Occurrence.**—This metal was discovered by Cronstedt, in 1751, in a copper-colored mineral, to which, having failed in attempting to extract copper from it, the miners had applied in derision the name *kupfernickel*.

and from which the name nickel has been derived. Except in meteoric irons, nickel does not occur free in nature, but it is a constituent of many minerals. It occurs as *niccolite* (kupfernickel) $NiAs$, *gersdorffite* $NiS_2,NiAs_2$, *ullmannite* $Ni_2S_2,(AsSb)_2$, *nickel blende* $NiS$, *zaratite* $NiCO_3$ with nickel hydrate, and *morenosite* $NiSO_4 7,Aq$, etc.

**32. Preparation.**—In the extraction of metals from ores containing a large percentage of iron sulphide, as is generally the case with sulphurous nickel ores, advantage is taken of the fact that iron sulphide can be readily roasted to oxide

$$4FeS_2+11O_2 = 2Fe_2O_3+8SO_2$$

and the oxide fluxed as ferrous silicate by fusion with silica. This method of removing iron may also be employed with those nickel ores that contain no sulphur, by heating them with gypsum and coke, when the iron becomes converted into sulphide. When the iron has been removed, a mixture of sulphides of nickel and copper (should the latter be present in the ores) remains. This is completely oxidized by roasting in the air

$$2NiS+3O_2 = 2NiO+2SO_2$$

and the mixture of oxides of nickel and copper is treated with dilute sulphuric acid, which dissolves the copper oxide; the nickel oxide is made into a paste with charcoal, the paste is cut into cubes and heated to reduce the nickel. The commercial metal is more or less contaminated with sulphur, carbon, iron, etc.

The arsenical nickel ores are treated as described above for the removal of iron, and the speiss thus obtained, consisting essentially of nickel and arsenic, but also mostly of a little cobalt and copper, is treated by a wet method for the separation of the cobalt. This is effected by roasting the speiss to expel most of the arsenic, dissolving in $HCl$, peroxidizing the solution by bleaching powder, and neutralizing with chalk; in this way the iron is precipitated as basic ferric carbonate, and the remaining arsenic as ferric arsenate. $H_2S$ is passed through the solution to precipitate bismuth

and copper as sulphides, leaving cobalt and nickel in solution. The latter, having been boiled to expel the excess of $H_2S$, is neutralized with lime and bleaching powder, which precipitates the cobalt as $Co_2O_3$, leaving $Ni$ in solution, from which it may be precipitated by adding lime; it is reduced as described above. The $Co_2O_3$ becomes $Co_3O_4$ when ignited.

**33. Properties.**—Nickel is a pure silver-white, ductile, and malleable metal, which has a specific gravity of 8.6. It is exceedingly infusible, and possesses a great tenacity. At ordinary temperature it is magnetic, but loses this property when heated to above 250°. This metal owes its value in the useful arts, in the first place, to its property of imparting a white color to the alloys of copper and zinc, with which it forms the alloy so well known under the name of *German silver;* and, second, to the ease with which it can be deposited by electrolysis on other metals (a process known as *electroplating*) as a shining and coherent film, which successfully resists the influence of the atmosphere for a considerable time. Nickel crucibles and dishes are frequently used in the laboratory as substitutes for those of silver and platinum, being much cheaper though not so durable. It has been found possible to weld sheet nickel on iron and steel plates, and vessels for various purposes are manufactured of such plates, which possess the advantages of not being liable to rust and of resisting vegetable acids. Steel containing nickel is, as has been previously mentioned, exceptionally hard.

Alloys of copper with nickel and zinc, or with nickel alone, are used in this country, Germany, Belgium, and Switzerland for the manufacture of small coins. The advantages of nickel coins are, *first*, that nickel being more expensive than copper, the coins can be made smaller for the same value, and are consequently more convenient to handle; *second*, that the alloy is hard and therefore wears well; and *third*, that its manufacture not only requires skilled workmen, but also powerful machines, facts that offer a certain safeguard against counterfeiting.

## COMPOUNDS OF NICKEL.

**34. Nickel Oxides.**—A monoxide (*nickelous oxide*) $NiO$ and a sesquioxide $Ni_2O_3$ are known. Nickelous oxide is an ash-gray powder, which is obtained by strongly calcining the nitrate or carbonate of nickel. On adding potassium hydrate to a nickel salt, an apple-green precipitate of nickel hydrate $Ni(OH)_2$ is formed.

**Nickel sesquioxide** $Ni_2O_3$ may be obtained by moderately calcining the nitrate. It is black. When chlorine gas is passed into water holding nickel hydrate in suspension, a dark-brown powder is obtained, which is the hydrate of the sesquioxide. This hydrate may also be obtained by precipitating a nickel salt with a mixture of potassium hydrate and an alkaline hypochlorite.

When strongly calcined, nickel sesquioxide abandons part of its oxygen and is changed into monoxide. Treated with hydrochloric acid, it yields nickel chloride, and chlorine is disengaged:

$$Ni_2O_3 + 6HCl = 2NiCl_2 + 3H_2O + Cl_2$$

**35. Nickel Chloride.**—Nickel chloride $NiCl_2$ may be obtained anhydrous by the action of chlorine on nickel filings; it is volatile at a dull-red heat, and sublimes in golden-yellow scales. The hydrated chloride is formed by the action of boiling water on the anhydrous salt, or by the action of hydrochloric acid on either oxide or carbonate of nickel. Its solution is green, and after proper concentration deposits beautiful green crystals, which contain $NiCl_2, 6Aq$.

**36. Nickel Sulphate.**—Nickel sulphate $NiSO_4, H_2O, 6Aq$ is deposited in fine emerald-green prisms, isomorphous with magnesium sulphate, when its solution is allowed to evaporate spontaneously below 15°. There is another sulphate containing $6H_2O$ which is dimorphous. When deposited between 20° and 30° it crystallizes in octahedrons, but when its solution is made to crystallize between 60° and 70°, monoclinic crystals are obtained isomorphous with the corresponding sulphates of zinc and cobalt.

Nickel sulphate dissolves in three times its weight of water at 10°.

**37.** Four **sulphides of nickel** are known—$Ni_2S$, $NiS$, $Ni_3S_4$, and $NiS_2$. $NiS$ is found native as *capillary pyrites*, and is obtained as a black precipitate by the action of an alkaline sulphide on a salt of nickel; like cobalt sulphide, it is almost insoluble in $HCl$, but ammonium disulphide dissolves it to a dark-brown liquid.

**38. Nickel Carbonyl.**—Nickel carbonyl $Ni(CO)_4$ is a colorless liquid of specific gravity 1.3, which boils at 43° and crystallizes at $-25°$. It is prepared by passing dry $CO$ through a tube containing finely divided nickel that has been reduced from $NiO$ by heating it in hydrogen at 400°. The $Ni(CO)_4$ is condensed from the excess of $CO$ used by passing the gas through a tube surrounded by ice water. It is insoluble in water, but dissolves in alcohol, benzene, and chloroform. Its vapor decomposes at 150° into $CO$ and $Ni$, which latter is deposited in the form of a mirror on the sides of the vessel; it is a powerful reducing agent.

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## MANGANESE.

*Symbol Mn. Atomic weight 54.8. Valence II, III* (?), *IV, VI, and VII* (?).

**39. History and Occurrence.**—Manganese was discovered by Scheele and Bergmann in 1774, in a mineral known as *braunstein*. Owing to its being confounded with magnetic iron, this mineral had received the Latin name of this substance, i. e., *magnesia nigra;* whence the name magnesium first was assigned to the new metal. This name was afterwards changed to manganese, to distinguish it from true magnesium obtained from magnesia alba. Manganese is found chiefly as *pyrolusite* $MnO_2$, *braunite* $Mn_2O_3$, and *manganese spar* $MnCO_3$. Manganese sulphide, arsenide, and silicate are also known as minerals. The metal itself has not been applied to any very useful purpose in the arts.

**40. Preparation and Properties.** — Manganese is obtained by reducing its oxide by charcoal at a high temperature. It is a grayish-white, hard, and brittle metal, and has a specific gravity of 8. It is feebly magnetic and difficult to fuse (1,900°). It oxidizes readily in the air.

Manganese dissolves easily in diluted hydrochloric and sulphuric acids, $Mn$ displacing $H_2$, like $Fe$ and $Cr$. It resembles iron in its tendency to combine with carbon at a high temperature to form a compound corresponding with cast iron, and in this form the manganese is not oxidized by air.

*Spiegeleisen* and *ferromanganese* are alloys containing iron, manganese, and carbon, and are largely used in the production of steel.

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## COMPOUNDS OF MANGANESE.

**41. Manganese Dioxide.**—*Manganese dioxide*, or *peroxide*, $MnO_2$ is the chief compound in which manganese is found in nature, and it is also the source from which practically all manganese compounds are obtained. Its chief mineral form is pyrolusite, which forms steel-gray prismatic crystals of specific gravity 4.9; but it is also found amorphous, as *psilomelane*, and in the hydrated state as *wad*. In commerce pyrolusite is known as black manganese, or simply manganese, and is largely imported from Germany, Spain, and other countries for use in manufacturing bleaching powder or glass. It is also used, as has been previously mentioned in Art. **10**, *Inorganic Chemistry*, Part 1, as a cheap source of oxygen, which it evolves when heated to redness, without fusing, leaving the red *oxide of manganese* $Mn_3O_4$. Manganese dioxide is an indifferent oxide, and does not combine with acids. Strong $HCl$, however, dissolves it, giving a brown solution from which water precipitates a brown oxychloride. If the brown solution, which probably contains $Mn_2Cl_6$ and $MnCl_4$, is heated, it evolves $Cl_2$ and becomes colorless $MnCl_2$. Nitric acid is almost without action on $MnO_2$. Strong sulphuric acid evolves oxygen from it:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$

Even dilute sulphuric acid produces the same change if some substance ready to combine with oxygen is added, as, for instance, ferrous sulphate or oxalic acid. Hence, a mixture of $MnO_2$ and $H_2SO_4$ is frequently used as an oxidizing agent.

When heated in hydrogen, the oxides of manganese are not reduced to the metal, like those of iron, but are converted into $MnO$.

**42. Manganous Oxide.** — Manganous oxide $MnO$, obtained in the way mentioned above, is a greenish powder, but it may also be obtained in transparent, emerald-green crystals. It easily absorbs oxygen from the air. It is a basic oxide, dissolving in acids to form the manganous salts. It has been found in nature in manganiferous dolomite.

**43. Manganic Oxide.**—Manganic oxide, or *manganese sesquioxide* $Mn_2O_3$, is found in the mineral *braunite* in octahedral crystals. By its general appearance it might be mistaken for $MnO_2$, but it dissolves in moderately strong sulphuric acid, forming a red solution of manganic sulphate $Mn_2(SO_4)_3$.

Manganic oxide is a feebly basic oxide. It may be obtained by heating any of the oxides of manganese to redness in a current of oxygen, while $Mn_3O_4$ is formed when any one of these oxides is heated in air. When a very small quantity of $MnO_2$ is added to melted glass, a purple color is imparted to the mixture, which is probably due to the formation of a manganic silicate. The amethyst is believed by some to owe its color to the same cause.

**44. Red Oxide of Manganese.**—Red oxide of manganese $Mn_3O_4$ is the most stable of the oxides of this metal, and is formed when either of the others is heated in air. Thus obtained, it has a brown or reddish color; but it is found in nature as the black mineral hausmannite.

**45. Manganic Anhydride.**—Manganic anhydride $MnO_3$ is formed in small quantities by dropping a solution

of potassium permanganate in concentrated $H_2SO_4$ on dry $Na_2CO_3$, and condensing the pink cloud that arises in a tube cooled by a mixture of ice and salt. It is a red, amorphous mass, yielding manganic acid in contact with water.

**46. Permanganic Anhydride.**—Permanganic anhydride $Mn_2O_7$ is a red, oily liquid formed when potassium permanganate is decomposed by strong sulphuric acid:

$$K_2Mn_2O_8 + 2H_2SO_4 = 2KHSO_4 + Mn_2O_7 + H_2O$$

It decomposes slowly, even at common temperatures, evolving oxygen together with violet vapor of $Mn_2O_7$. When heated, it decomposes with explosion. It is a most powerful oxidizing agent, setting fire to most combustible bodies. In contact with water, it yields permanganic acid $H_2Mn_2O_8$.

**47. Manganous Hydroxide.**—Manganous hydroxide $Mn(OH)_2$ is obtained as a white precipitate when an alkali is added to a manganous salt out of contact with air. When exposed to air, it rapidly becomes brown, changing into manganic hydroxide.

**48. Manganic Hydroxide.**—Manganic hydroxide $Mn_2O_2(OH)_2$ may be considered as $Mn_2O_3$ in which $O$ has been replaced by $(OH)_2$, or as $Mn_2O_3, H_2O$ (hydrated manganese sesquioxide). It occurs native in dark-gray crystals as the mineral *manganite*, associated with $MnO_2$, from which it differs by giving a brown instead of a black streak on unglazed earthenware. Moreover, on boiling it with dilute nitric acid, part of it is dissolved as manganous nitrate, leaving a hydrated manganese dioxide, which dissolves to a brown solution when thoroughly washed. A hydrated manganese dioxide is also precipitated when chloride of lime is added to a manganous salt.

**49. Manganic Acid.**—Manganic acid $H_2MnO_4$ has not yet been obtained, but a number of manganates are known that are isomorphous with the sulphates and chromates.

**50. Potassium Manganate.**—Potassium manganate $K_2MnO_4$ is obtained by fusing $MnO_2$ with potash, according to the equation:

$$3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O$$

If an oxidizing agent, such as air or niter, is present, the $Mn_2O_3$ is also converted into $K_2MnO_4$:

$$2Mn_2O_3 + 8KOH + 3O_2 = 4K_2MnO_4 + 4H_2O$$

**51. Sodium Manganate.**—Sodium manganate $Na_2MnO_4$, which is obtained by heating manganese dioxide with sodium hydroxide, is used in its aqueous solution for disinfecting purposes, and is known commercially under the name of *Condy's green disinfecting fluid.* It also finds employment in the manufacture of oxygen and as a bleaching agent.

Sodium manganate, as well as potassium manganate, dissolves in water containing soda or potash and forms a green liquid. If either of these manganates is dissolved in pure water, it decomposes and yields a red permanganate:

$$3Na_2MnO_4 + 2H_2O = Na_2Mn_2O_8 + MnO_2 + 4NaOH$$

Barium manganate forms the pigment known as *Cassel green.*

Manganous acid is not known.

**52. Permanganic Acid.**—Permanganic acid $H_2Mn_2O_8$ has been obtained in a crystalline state by decomposing barium permanganate with sulphuric acid and evaporating the solution in vacuo. It is thus obtained as a brown substance, which easily dissolves in water, forming a red liquid, which decomposes at about 32°, evolving oxygen and depositing manganese dioxide.

**53. Potassium Permanganate.**—Potassium permanganate $K_2Mn_2O_8$ is an important salt. It dissolves in 20 parts of cold water, forming a purple solution, which becomes green $K_2MnO_4$ by contact with many substances capable of taking up oxygen. When crystallized permanganate is heated to about 240°, it gives manganate, thus:

$$K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2$$

Potassium permanganate is prepared by heating to dull redness a mixture of manganese dioxide, potassium hydroxide, and potassium chlorate. After cooling, the product is treated with boiling water, and when the liquid has assumed a purple color, it is decanted, and, after neutralization by nitric acid, is evaporated at a gentle heat. On cooling, it deposits crystals that may be dried on a porous tile. These crystals are red by transmitted light, but reflect a dark-green color.

Potassium permanganate is remarkable for its great coloring power. A very small quantity of it produces an intense red color to a large quantity of water. Its solution in water is easily decomposed and bleached by a ferrous salt. If, for instance, a very small piece of iron wire is dissolved in diluted sulphuric acid, the solution of ferrous sulphate so produced will decolorize a large volume of a weak solution of the permanganate, being at the same time converted into ferric sulphate:

$$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4$$
$$= K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

Many organic substances are easily oxidized by potassium permanganate, and this is especially the case with the offensive emanations from putrescent organic matter. Hence, it is extensively used, under the name of *Condy's red disinfecting fluid*, in cases where a solid or liquid substance is to be effectively deodorized.

The oxidizing power of potassium permanganate may be strikingly illustrated by pouring a little glycerine into a cavity made in a small heap of finely powdered crystals of potassium permanganate on a glass plate; the glycerine slowly sinks into the permanganate, and after a very little while bursts into vivid combustion.

**54. Sodium Permanganate.**—Sodium permanganate $Na_2Mn_2O_6$, being cheaper than potassium permanganate, is very frequently used as a disinfectant. It is prepared by heating $MnO_2$ with $NaOH$ to dull redness for about 48 hours

in a flat vessel, the mass thus obtained being then boiled with water in order to convert the manganate obtained into permanganate:

$$3Na_2MnO_4 + 2H_2O = Na_2Mn_2O_8 + MnO_2 + 4NaOH$$

**55. Chlorides of Manganese.**—Three chlorides of manganese, corresponding with the three oxides of manganese, are known; namely, $MnCl_2$, $Mn_2Cl_6$, and $MnCl_4$. Apparently, only the first chloride can be obtained in the pure state, the others forming solutions that are easily decomposed with the evolution of chlorine.

By dissolving potassium permanganate in concentrated sulphuric acid and adding fused sodium chloride, a remarkable greenish-yellow gas is obtained, which gives purple fumes with moist air, and is decomposed by water, yielding a red solution containing hydrochloric and permanganic acids. It, therefore, must contain manganese and chlorine, and is sometimes regarded as the *perchloride of manganese* $MnCl_7$; but it is more probably an oxychloride of manganese.

**Manganous chloride** $MnCl_2$ is obtained in large quantities as a waste product in the preparation of chlorine for the manufacture of bleaching powder.

**Manganic chloride** $Mn_2Cl_6$ is formed when precipitated manganic oxide is immersed in cold concentrated hydrochloric acid, the oxide then dissolving quietly without the evolution of gas. Heat decomposes manganic chloride into manganous chloride and free chlorine.

**56. Manganous Sulphate.**—Manganous sulphate $MnSO_4,7Aq$ is prepared by dissolving manganous carbonate $MnCO_3$ in sulphuric acid. The properly concentrated rose-colored solution deposits, between 0° and 6°, oblique rhombic prisms, isomorphous with green vitriol and containing 7 molecules of water.

Between 7° and 20°, manganous sulphate crystallizes with 5 molecules of water, like cupric sulphate, with which it is then isomorphous. Between 20° and 30°, it is deposited in

oblique rhombic prisms, which then contain only 4 molecules of water.

All of these crystals are pink-colored, and their color is deeper the more water of crystallization they contain; all of them are extremely soluble in water.

**57. Manganous sulphide** $MnS$ occurs native as ***manganese blende*** in steel-gray masses. It may be obtained as a greenish powder by heating one of the oxides of manganese in a current of $H_2S$. When precipitated by alkaline sulphides from manganese salts, it has a pink color and contains water. When the pink precipitate is boiled with an excess of alkaline sulphide, it becomes a green, crystalline powder $3MnS, H_2O$. The manganous sulphide has a tendency to form soluble compounds with the alkaline sulphides, so that a solution of manganese often requires boiling with ammonium sulphide before a precipitate is formed. It dissolves easily in $HCl$.

**Manganese disulphide** $MnS_2$ is found in crystalline form as *hauerite* in Hungary.

**58.** Manganese, though more nearly allied to iron than to any other metal, is parted from it by the greater stability of the manganous salts, which are less easily oxidized than the ferrous salts, as well as by the considerably greater stability of the manganates than the ferrates, and by the existence of the permanganates, which have no parallel in the iron series.

The chlorides of manganese give a green color to a colorless flame.

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## CHROMIUM.

*Symbol Cr. Atomic weight 52.4. Valence II, III, IV, and VI.*

**59. History and Occurrence.**—Chromium was discovered in 1797 by Vauquelin, in a mineral from Siberia, known as *crocoite*, which is a chromate of lead. It derives its name from the Greek χρῶμα, *chroma*, meaning "color," in allusion

to the varied colors of its compounds, on which their uses in the arts chiefly depend. It occurs in nature in the mineral *chromite*, or *chrome iron*, a combination of chromium oxide and ferrous oxide, and also as lead chromate in the mineral *crocoite*. It is chiefly found in this country, Sweden, Russia, and Hungary. It forms the coloring matter of the precious stone emerald, and occurs in meteoric irons.

**60. Preparation and Properties.**—Chromium is prepared by reducing its oxide by charcoal; or, better, by reducing the chloride by zinc or magnesium. By the former method, it is obtained as a steel-gray mass, highly infusible and extremely hard; by the latter, as a grayish-green, lustrous powder, composed of tetragonal octahedrons, of specific gravity 6.8. It is not magnetic, and although it is unaltered when heated in dry air, burns readily in oxygen. Metallic chromium has not received any useful application in the arts so far.

## COMPOUNDS OF CHROMIUM.

**61. Oxides of Chromium.**—Three oxides of chromium are known to exist in the separate state; namely, *chromic oxide* $Cr_2'''O_3$, *chromium dioxide* $Cr^{iv}O_2$, and *chromic anhydride*, or *trioxide* $Cr^{vi}O_3$. *Monoxide of chromium*, or *chromous oxide* $Cr''O$, is known in the hydrated state, and *perchromic acid* $H_2Cr_2O_8$ is believed to exist in solution. The chromous salts correspond with the ferrous salts, but are much more susceptible of oxidation.

*Chromic trioxide*, or *anhydride*, also known as *chromic acid*, is the most important of these; it is obtained by mixing a saturated solution of potassium bichromate with its own volume of strong sulphuric acid. On cooling, splendid crimson needles of the trioxide crystallize out. It is deliquescent in damp air, and is decomposed by a heat of about 250° into oxygen and chromic oxide.

Chromic trioxide is a powerful oxidizing agent; most organic substances, even paper, will reduce it to chromic oxide, and alcohol poured on it is at once inflamed.

A mixture of *potassium bichromate* $K_2Cr_2O_7$ and sulphuric acid is employed for bleaching some oils, the coloring matter being oxidized at the expense of the chromic acid, and chromic sulphate being produced:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3O + 4H_2O$$

The bichromate itself evolves oxygen when heated to bright redness, being first fused (at about 400°) and then decomposed:

$$4K_2Cr_2O_7 = 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

Heated with strong $HCl$, it evolves chlorine.

The oxidizing effect of the potassium bichromate, under the action of light, upon gelatine and albumin, receives very important applications in photography.

**Sodium bichromate** $Na_2Cr_2O_7, 2H_2O$ is much more soluble than the potassium salt, requiring only an equal weight of water, and is now often substituted for $K_2Cr_2O_7$.

**Chromic acid** $H_2CrO_4$ is not known in pure form. Its salts, the chromates, are isomorphous with the sulphates.

**62. Potassium Chromate.**—Potassium chromate $K_2CrO_4$ is formed by adding potassium carbonate to the red solution of potassium bichromate until its red color changes to a yellow one, when it is evaporated and allowed to crystallize. It forms yellow prismatic crystals, and is five times as soluble in water as potassium bichromate, yielding an alkaline solution that is partly decomposed by evaporation, with the formation of the bichromate. Acids, even carbonic, change its solutions from yellow to red, owing to the production of bichromate. Potassium chromate assumes a red color when heated, but changes back to yellow on cooling.

**63. Potassium Trichromate.**—Potassium trichromate $K_2O, 3CrO_3$ has been obtained in red crystals by adding nitric acid to the bichromate.

The student will notice that the chromates of potassium take a somewhat exceptional position. The yellow, or normal, chromate $K_2CrO_4$ is formed on the model of imaginary chromic

acid $H_2CrO_4$. The red chromate, or potassium bichromate, is not a true acid salt, as it contains no hydrogen; it is sometimes called *anhydrochromate* and written $K_2CrO_4, CrO_3$. The trichromate would then be $K_2CrO_4, 2CrO_3$.

**64. Barium Chromate.**—Barium chromate $BaCrO_4$ is used in painting under the name of *yellow ultramarine.*

**Chrome yellow** is the *chromate of lead* $PbCrO_4$; it may be obtained by mixing dilute solutions of lead acetate and potassium chromate. It finds wide employment in the arts, especially in calico printing and painting, and is frequently used in the laboratory as a source of oxygen for the analysis of organic substances, since, when heated, it fuses to a brown mass, which evolves oxygen at a red heat. Chrome yellow is a poisonous salt, and its use in the candy industry as a coloring matter cannot be too strongly condemned.

**Orange chrome** is a *basic lead chromate* $PbCrO_4, PbO$ and may be obtained by boiling the yellow chromate with lime:

$$2PbCrO_4 + CaO = PbCrO_4, PbO + CaCrO_4$$

In dyeing and calico printing the material is dyed with the ordinary yellow lead chromate and then dipped in a bath of lime water, by which the yellow is converted into a beautiful orange color.

**Silver chromate** $Ag_2CrO_4$ is obtained as a red precipitate when silver nitrate is added to potassium chromate. When $K_2Cr_2O_7$ is added gradually to $AgNO_3$ a scarlet precipitate of *silver bichromate* $Ag_2Cr_2O_7$ is obtained.

**65. Chromic Oxide.**—Chromic oxide, or *sesquioxide of chromium* $Cr_2O_3$, is valuable as a green color, and, as it is not decomposed by heat, it is largely used for coloring glass and china. It is prepared by heating potassium bichromate with one-fourth of its weight of starch, the carbon of which removes oxygen, leaving a mixture of chromic oxide with potassium carbonate, which may be removed by washing with water. When hydrated chromic acid is strongly heated, it loses its water and exhibits a sudden glow, becoming

darker in color and insoluble in acids that previously dissolved it easily; in this respect it resembles alumina and ferric oxide., Like these oxides, the chromic oxide is a feeble base; it is remarkable for forming two classes of salts, which, though they have the same composition, differ in the color of their solution and other properties. There are, for instance, two modifications of chromic sulphate—the green sulphate $Cr_2(SO_4)_3, 5Aq$, and the violet sulphate $Cr_2(SO_4)_3, 15Aq$. The solution of the latter becomes green when boiled, being converted into the former.

**Chrome alum** forms octahedrons of $KCr(SO_4)_2, 12H_2O$, of a dark-purple color, which contain the violet modification of the sulphate; and if its solution in water is boiled, its purple color changes to green and the solution refuses to crystallize. It is obtained as a secondary product in different chemical manufactures, and may be prepared by the action of sulphur dioxide on a mixture of potassium bichromate and sulphuric acid:

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = 2KCr(SO_4)_2 + H_2O$$

The anhydrous chromic sulphate forms red crystals, which are insoluble in water as well as in acids. *Guignet's green*, a pigment frequently used in painting and calico printing, is hydrated $Cr_2O_3$, prepared by heating $K_2Cr_2O_7$ with 3 parts of boric acid (when oxygen is evolved) and washing the product until it is free from potassium borate. $Cr_2O_3$ combines with the oxides of the magnesium group of metals to form very insoluble and infusible compounds, crystallizing in octahedrons; for instance, $ZnO, Cr_2O_3$, as $MnO, Cr_2O_3$, and $FeO, Cr_2O_3$; which compounds have been termed *chromites*.

**66. Chromic Hydroxide.**—Chromic hydroxide $Cr_2(OH)_6$ or $Cr(OH)_3$ is thrown down by alkalies from solutions of chromic salts, such as chrome alum, as a greenish-blue precipitate. It dissolves sparingly in ammonia to a pink solution, from which chromic oxide is precipitated by boiling. Potash dissolves it to a fine green solution, which becomes gelatinous when boiled, from precipitation of chromic oxide.

**67. Chromium Dioxide.**—Chromium dioxide $CrO_2$ is obtained when potassium bichromate is reduced by nitrogen dioxide $N_2O_3$ or sodium thiosulphate as a brown precipitate. This precipitate consists of a mixture of water and chromium dioxide, which, on heating to 250°, becomes a black powder, and at 300° evolves oxygen and becomes $Cr_2O_3$.

**68. Chromous Oxide.**—Chromous oxide $CrO$ is not known in the pure state, but is precipitated as brown hydrate when chromous chloride is decomposed by potash. It absorbs oxygen eagerly, becoming converted into $CrO, Cr_2O_3$. Chromous oxide is a feeble base.

**69. Perchromic Acid.**—Perchromic acid $H_2Cr_2O_8$ is believed to exist as the blue solution obtained by the action of $H_2O_2$ (hydrogen peroxide) upon a solution of chromic acid. If an acid solution of potassium chromate is treated with hydrogen peroxide, a blue liquid is obtained. If this solution is agitated with ether and allowed to stand, a bright blue layer, which is believed to be a solution of perchromic acid in ether, gathers on the surface of the liquid.

**70. Chromic Chloride.**—Chromic chloride $CrCl_3$ is the most important compound of chromium and chlorine. It is obtained by passing chlorine gas over an ignited and perfectly dry mixture of chromium and charcoal. A sublimate of brilliant scales, having the color of peach blossoms, is thus obtained, which is almost insoluble in cold and only sparingly soluble in boiling water, forming with the latter a green solution. It is unaltered by ordinary reagents. A soluble violet modification is produced by heating the green solution in a current of hydrochloric acid.

The chlorine of the violet solution is completely precipitated by silver nitrate; that of the green solution is only partially precipitated.

**71. Chromous Chloride.**—Chromous chloride $CrCl_2$ may be obtained by reducing chromic chloride by hydrogen

at a moderate heat. It is a white, crystalline substance, soluble in water, forming a blue solution, which by absorption of oxygen rapidly changes its color to green.

**72. Chromyl Chloride.**—Chromyl chloride $CrO_2Cl_2$ is obtained by heating a previously fused mixture of common salt and potassium bichromate with sulphuric acid; abundant red vapors are disengaged, and condensed to a blood-red liquid. Chromyl chloride boils at 116.8°. On contact with water it decomposes into hydrochloric acid and chromic anhydride:

$$CrO_2Cl_2 + H_2O = CrO_3 + 2HCl$$

**73. Chromic Perfluoride.**—Chromic perfluoride $CrF_6$ is obtained by distilling lead chromate and calcium fluoride (fluorspar) with sulphuric acid, according to the equation:

$$PbCrO_4 + 3CaF_2 + 4H_2SO_4$$
$$= PbSO_4 + 3CaSO_4 + 4H_2O + CrF_6$$

An orange vapor is evolved, which condenses to a blood-red liquid, boiling at a temperature but little above the ordinary temperature of the laboratory, fuming in contact with moist air, and decomposed by water, forming hydrofluoric and chromic acids.

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## GENERAL REVIEW OF IRON, COBALT, NICKEL, MANGANESE, AND CHROMIUM.

**74.** The student will have noticed many points of resemblance in the chemical properties of these metals. They are all capable of decomposing water at red heat, and easily displace hydrogen from hydrochloric acid. Each of them forms a base by combining with 1 atom of oxygen, and these oxides produce salts that have the same crystalline form. All these oxides, except that of nickel, easily absorb oxygen from the air, and are converted into sesquioxides. The sesquioxide of nickel is very feebly basic, while that of cobalt is slightly more basic; the sesquioxide of manganese is a stronger base,

and the basic properties of the sesquioxides of chromium and iron are very decided. Nickel does not exhibit any tendency to form a well marked acid oxide, but the existence of an acid oxide of cobalt is suspected; and iron, manganese, and chromium form undoubted acid oxides with 3 atoms of oxygen. Nickel is only known to form one compound with chlorine; cobalt and manganese form, in addition to their protochlorides, very unstable perchlorides known only in solution, but iron and chromium form very stable volatile perchlorides. The metals forming this group are all divalent in their protoxides and the corresponding salts, and are found associated in natural minerals, which is especially the case with iron, manganese, cobalt, and nickel. They all require a very high temperature for their fusion. Iron and chromium connect this group with aluminum, their sesquioxides being isomorphous with alumina, and their perchlorides volatile, like aluminum chloride. In the periodic table (see Art. **39,** *Inorganic Chemistry*, Part 3), *Cr* falls in Group VI, since its highest salt-forming oxide is $CrO_3$; *Mn* forms salts corresponding with $Mn_2O_7$ (permanganates), and is therefore in Group VII. *Fe*, *Co*, and *Ni* are placed in Group VIII, although oxides of the type $RO_4$ have yet to be discovered.

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## MOLYBDENUM.

*Symbol Mo. Atomic weight 95.6. Valence II, III, IV, V, and VI.*

**75. Occurrence and Properties.**—This metal occurs in small quantity as sulphide, or *molybdenite*, and as lead molybdate, or *wulfenite*. It is prepared by reducing molybdic oxide $MoO_3$ by a current of hydrogen at a high temperature. It is a white, very hard, and brittle metal, and almost infusible. It has a specific gravity of 8.62, and oxidizes, when heated in the air, to molybdic oxide. It forms five oxides: $MoO$, $Mo_2O_3$, $MoO_2$, $Mo_2O_5$, and $MoO_3$.

**76. Molybdic Trioxide.**—Molybdic trioxide $MoO_3$, commonly called *molybdic acid*, is obtained by roasting native molybdenite $MoS_2$. The roasting is conducted at moderate temperature, and the resulting oxide is dissolved in ammonia and the solution filtered. On evaporation and cooling, crystals of ammonium molybdate are obtained, which yield molybdic oxide when strongly heated in the air.

Molybdic oxide is a white, fusible, and volatile powder; it is only slightly soluble in water, its solution being acid. It is the anhydride of an acid that forms a series of rather complicated salts, the most important of which is a molybdate of ammonia, having the composition $(NH_4)_2MoO_4$. It is employed in the laboratory as a test for phosphorus.

**77.** Molybdenum forms four chlorides; namely, $MoCl_2$, $MoCl_3$ or $Mo_2Cl_6$, $MoCl_4$, and $MoCl_5$ or $Mo_2Cl_{10}$.

The *pentachloride* $MoCl_5$ is obtained when pure metallic molybdenum is heated for some time in a stream of chlorine. If this pentachloride is heated to about 250° in a stream of hydrogen, it is reduced to the red, difficultly volatile *trichloride* $MoCl_3$, or $Mo_2Cl_6$; and this compound heated to redness in an atmosphere of carbon dioxide free from oxygen, is resolved according to the equation

$$Mo_2Cl_6 = MoCl_2 + MoCl_4$$

into the yellow *dichloride*, which remains in the tube, and the brown tetrachloride, which either sublimes or is carried forward by the stream of gas.

Of these four chlorides, the pentachloride is the only one that crystallizes distinctly, and melts and volatilizes without decomposition. The pure pentachloride is black, and its vapor has a dark, brown-red color. The yellow dichloride and the red trichloride, which latter closely resembles amorphous phosphorus, have been obtained only in the amorphous state. In an atmosphere of carbon dioxide, the dichloride bears a bright-red heat without melting or volatilizing; the trichloride, under the same circumstances, is resolved into dichloride and tetrachloride, which, when again heated,

splits up into pentachloride which sublimes, and trichloride which remains behind.

The dichlorides and trichlorides are permanent at ordinary temperatures in the atmosphere and insoluble in water; the tetrachloride and pentachloride, on the other hand, are rather unstable, being very susceptible to the action of oxygen and moisture.

The dichloride is insoluble in nitric acid, which readily dissolves all the other chlorides. The dichloride dissolves easily when heated with hot hydrochloric acid, and crystallizes therefrom on cooling in long, yellow, lustrous needles, having the composition $Mo_2Cl_4,3H_2O$, which, when heated to 100°, give off 2 molecules of $H_2O$.

The *bromides* of molybdenum correspond in composition with the chlorides.

**78.** Three sulphides of molybdenum are known: $MoS_2$, $MoS_3$, and $MoS_4$, the last two of which are acid sulphides forming salts.

**Molybdic sulphide,** or disulphide, $MoS_2$ occurs native as molybdenite, as has been previously mentioned; it thus occurs in masses of tabular crystals that possess a strong metallic luster and steel-gray color. These crystals leave a gray streak on paper, similar to graphite. The same compound is produced artificially by heating either of the higher sulphides or by igniting the trioxide with sulphur. When roasted in contact with the air, it is converted into trioxide.

The **trisulphide** $MoS_3$ is obtained by passing hydrogen sulphide into a concentrated solution of an alkaline molybdate and precipitating with an acid. It is a dark-brown powder which is slowly soluble by alkalies, and more easily by alkaline sulphides, forming sulphur salts called *thiomolybdates.* The thiomolybdates of the alkali metals, alkaline earths, and magnesium are soluble in water, forming solutions of a fine red color.

The **tetrasulphide** $MoS_4$ is also an acid sulphide, forming salts known as *perthiomolybdates.*

**79. Molybdous Salts.**—Molybdous salts, obtained by dissolving molybdous oxide $MoO$ in acids, are opaque and nearly black in color. They yield with hydrogen sulphide a dark-brown precipitate soluble in ammonium sulphide; with alkalies and alkaline carbonates, a brownish-black precipitate of molybdous hydroxide, easily soluble in acid potassium carbonate or in ammonium carbonate; with potassium ferrocyanide, a dark-brown precipitate; with sodium phosphate, a white precipitate.

Solutions of molybdic salts have a reddish-brown color. When heated in the air, they have a tendency to become blue by oxidation. If they are brought in contact with metallic zinc, they at first change their color to brown and then yield a black precipitate of molybdous hydroxide. Though their reactions with alkalies and hydrogen sulphide are similar to those of molybdous salts, precipitates are easily recognized by being of a much lighter color.

## TUNGSTEN.

*Symbol W. Atomic weight 184. Valence IV and VI.*

**80. Occurrence and Preparation.**—Tungsten occurs in nature in a number of minerals and is found, as a rule, associated with tin ores. Its symbol $W$ is derived from the mineral *wolframite*, which is tungstate of iron and manganese, and from which this element was first obtained; it further occurs in *scheelite*, which is calcium tungstate; in *stolzite*, or *scheelitine*, which is lead tungstate; etc.

Metallic tungsten is obtained by reducing tungstic oxide $WO_3$ with either hydrogen or charcoal at a white heat as an iron-gray or black metal of specific gravity 19.1. It is extremely hard, very infusible, and unaffected by either hydrochloric or sulphuric acid, though it is converted into tungstic acid by the action of nitric acid. When tungsten is dissolved in steel, it forms an extremely hard alloy, known as *tungsten steel*, which is used in the manufacture of machinists' tools. One of the most peculiar properties of

tungsten is its ability to increase the magnetic power of the steel with which it is alloyed. A horseshoe magnet of ordinary steel, weighing 2 pounds, for instance, is generally considered of very good quality if it bears seven times its own weight, but a similar magnet made of an alloy of steel and tungsten is said to bear nearly twenty times its own weight.

## COMPOUNDS OF TUNGSTEN.

**81. Tungstate of Sodium.**—This is employed by calico printers as a mordant. It is obtained by fusing wolframite with sodium carbonate. Water extracts the sodium tungstate, which may be crystallized in rhomboidal plates having the composition $Na_2WO_4,2Aq$. When a solution of this salt is mixed with an excess of hydrochloric acid, *white hydrated tungstic acid* $H_2WO_4,Aq$ is precipitated, while hot solutions give a *yellow* precipitate of $H_2WO_4$; but if dilute hydrochloric acid is carefully added to a 5-per-cent. solution of sodium tungstate in sufficient proportion to neutralize the alkali, and the solution is then dialyzed, the sodium chloride passes through, and a pure aqueous solution of tungstic acid is left in the dialyzer. This solution is unchanged by boiling, and when evaporated to dryness, it forms vitreous scales, like gelatine, which adhere strongly to the dish. It redissolves in one-fourth of its weight of water, forming a solution of the rather high specific gravity 3.2. The solution has a bitter and astringent taste, and decomposes sodium carbonate with effervescence. It becomes green when exposed to air, from the deoxidizing action of organic dust floating in the air. When tungstic acid is heated, it loses water, changes its color to straw yellow, and becomes insoluble in acids.

**Barium tungstate** is sometimes employed as a substitute for white lead in painting.

The most characteristic property of tungstic acid is that of yielding a blue oxide, having the composition $WO_2,2WO_3$, when placed in contact with hydrochloric acid and metallic zinc.

Another very remarkable compound containing tungstic acid and soda is obtained when *sodium ditungstate* $Na_2W_2O_7,4H_2O$ is fused with tin. If the fused mass is treated with strong potash to remove free tungstic acid, washed with water, and treated with hydrochloric acid, yellow, lustrous, cubical crystals are obtained which are remarkable, among sodium compounds, for their resistance to the action of water, of alkalies, and of all acids but hydrofluoric. The composition of these crystals is supposed to be $Na_2O, WO_2, 2WO_3$; they are known as *gold*, or *saffron*, *bronze*. The corresponding potassium salt is *violet*, or *magenta*, *bronze*.

The **tungstoborates** are remarkable salts, containing $WO_3$ and $B_2O_3$ combined with metallic oxides. Their solutions have a very high specific gravity; that of cadmium tungstoborate, for instance, has the specific gravity of 3.6.

**82. Tungsten dioxide,** or *tungstous oxide*, $WO_2$ appears to be an indifferent oxide, and is obtained by reducing tungstic oxide with hydrogen at a low red heat, when it forms a brown powder, which is dissolved by boiling in solution of potash, hydrogen being evolved, and potassium tungstate formed.

**83. Tungsten trioxide,** or *tungstic oxide*, $WO_3$ is obtained by decomposing metallic tungstates with nitric acid, and heating the tungstic acid thus precipitated. It is a canary-yellow powder, becoming orange when heated and yellow again when cooled.

**84. Chlorides of Tungsten.**—When metallic tungsten is heated in chlorine the tungstic chloride $WCl_6$ sublimes in bronze-colored needles. When gently heated in hydrogen, it is converted into tetrachloride $WCl_4$, but if its vapor is mixed with hydrogen and passed through a glass tube heated to redness, metallic tungsten is obtained in a form in which it is not dissolved even by aqua regia, though it may be converted into potassium tungstate by potassium hypochlorite mixed with potash in excess. $WCl_6$ is also obtained in steel-blue needles, together with $WOCl_4$ and $WO_2Cl_2$ by the action of $PCl_5$ on $WO_3$.

**85. Tungsten disulphide** $WS_2$ is a black, crystalline substance resembling graphite; it may be obtained by heating a mixture of potassium ditungstate with sulphur, and washing with hot water.

**Tungsten trisulphide** $WS_3$ is a sulphur acid, obtainable as a brown precipitate by dissolving tungstic acid in an alkaline sulphide, and precipitating by an acid.

$WO_3$, like $MoO_3$, forms a large number of more or less complex salts with the alkali oxides and the pentoxides of arsenic, phosphorus, and vanadium, known as *tungsto-* and *molybdo-arsenates*, *phosphates*, and *vanadates*, respectively.

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## URANIUM.

*Symbol U. Atomic weight 240. Valence II, IV, and VI.*

**86. Occurrence and Preparation.**—The chief mineral used as a source of uranium is *pitchblende*, in which it occurs as $U_3O_8$.

When this is finely powdered and heated with sulphuric acid, the uranium is transformed partly into uranium sulphate $U(SO_4)_2$ and partly into uranyl sulphate $UO_2SO_4$, both of which are readily soluble in water. The oxide $U_3O_8$ is used in coloring porcelain black, and other uranium compounds are used for pigments and in the manufacture of colored glass.

That which was regarded as the metal from the time of the discovery of uranium by Klaproth, in 1789, until 1841, was in reality the dioxide $UO_2$. In 1841 Peligot showed that this contained oxygen by heating it mixed with charcoal in a current of chlorine gas, when carbon monoxide and dioxide were given off.

The pure metal may be prepared by strongly heating the tetrachloride $UCl_4$ with metallic sodium. The experiment is carried out in a crucible enclosed in a second crucible containing charcoal, so as to insure the exclusion of air. More recently it has been obtained by heating the oxides with carbon at the highest temperature attainable in the electric furnace.

**87. Properties.**—Uranium is a white metal, capable of taking a high polish, and is somewhat softer than steel. It combines directly with fluorine at ordinary temperatures; with chlorine, bromine, iodine, sulphur, and oxygen at a moderate heat; and with nitrogen at a bright-red heat. It decomposes water slowly at ordinary temperatures, and very rapidly at about 100°. Uranium mixed with carbon at high temperatures forms a carbide $U_2C_3$, and this carbide acts on water, forming a mixture of gaseous, liquid, and solid hydrocarbons.

## COMPOUNDS OF URANIUM.

**88. Oxides.**—The more important oxides are *uranium dioxide* $UO_2$ and *uranium trioxide* $UO_3$. The former is an extremely stable base, which enters into the composition of a well defined series of salts, the *uranyl salts;* e. g., $UO_2SO_4$, $UO_2(NO_3)_2$, $UO_2CO_3$, etc. The trioxide plays the part of an acid oxide, forming the *uranates*, of which the best known is *uranium yellow* $Na_2O,2UO_3$, obtained by adding caustic soda to a uranyl salt.

There are also oxides of more complex character, which are probably formed by the association of these two oxides, e. g., the black oxide $U_2O_5$ and the dark green $U_3O_8$.

**Uranium peroxide** $UO_4$ is perhaps the most stable body of this class; it may be obtained as a pale-yellow powder on adding hydrogen peroxide to a uranyl salt. The existence of *peruranates*, e. g., $K_4UO_8,10H_2O$, points possibly to a still higher oxide $UO_6$, which, however, has not been obtained so far.

**89. Sulphides.**—When heated, uranium combines directly with sulphur, forming *uranium disulphide* $US_2$, which, when reduced in hydrogen, yields *uranium sulphide* $US$. Oxysulphides also exist, and the precipitate formed when ammonium hydrosulphide is added to a uranyl salt is probably *uranyl sulphide* $UO_2S$.

**90. Chlorides.**—Uranium combines directly with chlorine to form *tetrachloride of uranium* $UCl_4$, some

*pentachloride* $UCl_5$ being produced at the same time. The tetrachloride is formed when an oxide of uranium mixed with carbon is heated in a stream of chlorine gas. It can be vaporized without decomposition, but the pentachloride easily gives off part of its chlorine. The dioxide $UO_2$ also combines directly with chlorine, forming a very stable uranyl chloride $UO_2Cl_2$, a yellow crystalline body that can be volatilized without decomposition.

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## REVIEW OF THE CHROMIUM FAMILY OF METALS.

**91.** The members of this family (chromium, molybdenum, tungsten, and uranium) exhibit great similarity in their tendency to form acid oxides of the type $RO_3$, and oxychlorides of the type $RO_2Cl_2$. They also enter into the composition of many complex salts analogous to the *phospho-molybdates* and the *boro-tungstates*. Sulphur, selenium, and tellurium belong to the same group, and form oxyacids of the same type.

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## BISMUTH.

*Atomic weight 208. Symbol Bi. Valence III and V.*

**92. History and Occurrence.**—Bismuth was first distinctly recognized by Basil Valentine in the fifteenth century. Agricola, in 1529, called it *bismetum*, and Paracelsus mentions it as *wismeat*. It was for a long time confounded with other metals, especially with lead, tin, and antimony. Pott, in 1739, first described its characteristic actions. This metal occurs in the metallic state in veins traversing gneiss, clay, slate, and other rocks, principally in Saxony, Germany, and Bohemia, Austria. It also occurs as oxide, forming the mineral *bismite;* as sulphide, or *bismuthinite;* as telluride, or *tetradymite;* and as carbonate, known as *bismuthite* or *bismutite.*

**93. Preparation and Properties.**—Bismuth is obtained on a large scale in the arts from the native bismuth by

placing this, mixed with the rocky gangue, in iron tubes slightly inclined, which are heated in a furnace. The bismuth melts and flows out at the lower ends of the tubes into suitable vessels, from which it is ladled into molds. The bismuth of commerce is mostly contaminated with arsenic, iron, and various other metals, from which it may be freed by fusion with potassium nitrate, by which the metals are oxidized. Chemically pure bismuth may be obtained by reducing bismuth nitrate $Bi(NO_3)_3$ with charcoal.

Bismuth is a hard, brittle, brilliant metal of a reddish-white color. It has a great tendency to crystallize on fusion; by melting a considerable quantity of it, allowing it to cool until a crust forms on the surface, piercing this and pouring out the metal that still remains liquid, crystals of great size and beauty may be obtained. Owing to a slight superficial oxidation, these crystals, as usually obtained, are beautifully iridescent. Bismuth has a specific gravity of 9.83; it melts at 264°, and expands one thirty-second of its bulk on solidifying. It may be distilled at a white heat. It is unaltered in dry air, but is tarnished in the presence of moisture. Strongly heated, it takes fire, burning with a bluish-white flame, and forming bismuthous oxide $Bi_2O_3$. Chlorine and nitric acid attack it readily, but hydrochloric and sulphuric acids, when cold, have no action on it.

Bismuth is used in the arts chiefly for forming alloys. *Rose's fusible metal* is composed of 1 part of lead, 1 of tin, and 2 of bismuth; it melts at 94°. *Lipowitz's fusible metal* contains 3 parts of cadmium, 4 of tin, 8 of lead, and 15 of bismuth; it melts at 64°. An alloy of lead and bismuth is used in the so called *permanent metallic pencils*. Bismuth is also employed in medicine.

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## COMPOUNDS OF BISMUTH.

**94. Oxides.**—The chief oxides are the yellowish *bismuthous oxide*, or *bismuth trioxide* $Bi_2O_3$, and the orange-red *bismuth pentoxide* $Bi_2O_5$. There is also a black *bismuth*

*dioxide* $Bi_2O_2$, obtained on adding caustic soda in presence of stannous chloride to the solution of its salts.

**Bismuthous oxide** is obtained by heating metallic bismuth in air. If this oxide is suspended in a strong solution of caustic potash and exposed to a stream of chlorine, it is transformed into red bismuthic acid, which, upon gentle ignition, yields the pentoxide. This oxide readily decomposes into the bismuthous oxide and oxygen when it is strongly heated, and, in the presence of hydrochloric acid, chlorine is evolved and bismuth chloride is formed :

$$Bi_2O_5 + 10HCl = 2BiCl_3 + 2Cl_2 + 5H_2O$$

**95. Bismuth Trisulphide.**—Bismuth trisulphide, or *bismuthous sulphide* $Bi_2S_3$, occurs native as bismuthinite. It is obtained as a black precipitate, on adding hydrogen sulphide to solutions of bismuth; but, unlike the solutions of arsenic and antimony, it is not soluble in solutions of the alkali sulphides. It forms, with metallic sulphides, salts called *sulpho-bismuthites*, some of which, as that of lead, or *kobellite* $Pb_3(BiS_3)_2$, and those of copper, called *emplectite* $Cu(BiS_2)_2$ and *wittichenite* $Cu_3(BiS_3)_2$, occur in nature.

**96. Bismuthous Chloride.**—Bismuthous chloride, or *bismuth trichloride* $BiCl_3$, may be formed by the direct action of chlorine on bismuth. It is a white, granular, deliquescent substance, fusible at 230°, and volatile at 435°. By contact with water it is decomposed, forming *bismuthyl chloride* $BiOCl$, also known as *bismuth oxychloride*.

**97.** The tri-fluoride, tri-bromide, and tri-iodide are similarly prepared, and in presence of water these yield precipitates of basic salts.

**98. Bismuth Nitrate.**—Most important among the bismuth compounds is the *nitrate* $Bi(NO_3)_3$, obtained by dissolving bismuth or its trioxide in nitric acid and the basic salts formed from it. If the acid solution of the nitrate is *largely* diluted with water, *basic nitrates* are obtained of composition varying with the amount of water used, or the temperature, or time during which the water is allowed to act. *Magistery*

*of bismuth*, *flake white*, and *Spanish white* are examples of mixtures of such basic nitrates, the general nature of which may be represented by the formulas: $Bi(OH)_2NO_3$, or $BiONO_3,H_2O$; $Bi_2O_2(OH)NO_3$; and $Bi_2O_2(NO_3)_2$. Such compounds, and those resulting from action of water or heat on bismuth sulphate, afford excellent illustrations of the composition of basic salts. They are salts in which part of the acid oxide has become displaced by the basic oxide, or hydroxide.

**99. Bismuth Sulphate.**—Bismuth sulphate $Bi_2(SO_4)_3$ separates out in white crystals when bismuthous oxide is dissolved in hot concentrated sulphuric acid and the solution is allowed to cool. By the action of water, the basic sulphate $Bi_2(OH)_4SO_4$ is precipitated according to the equation:

$$Bi_2(SO_4)_3 + 4H_2O = Bi_2(OH)_4SO_4 + 2H_2SO_4$$

and by heating, the basic sulphate $Bi_2O_2SO_4$ is formed; in either case two-thirds of the acid radical is thus removed from the original salt.

## ANTIMONY.

*Symbol Sb. Atomic weight 120. Valence III and V.*

**100. History and Occurrence.**—Antimony has been known for many hundred years; it was prepared in the pure state by Basil Valentine towards the end of the fifteenth century. It occurs in nature both free and in combination. The most abundant source of it is the sulphide known as *stibnite*, but it also exists in combination with oxygen in the minerals *valentinite*, *senarmontite*, and *cervantite*, with silver in *dycrasite;* and with silver and sulphur in *pyrargyrite* and *miargyrite*.

**101. Preparation and Properties.**—Antimony is obtained from the sulphide by heating it in covered pots with metallic iron:

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb$$

The excess of iron is removed by heating with charcoal and fluxes, such as sodium carbonate, and a further addition of the sulphide. The metal extracted in this way is contaminated with arsenic, iron, sulphur, and often lead or copper. It may be further purified by remelting with potash, and then on solidifying it shows fern-like markings due to crystallization, and is known as *star metal.*

Antimony is a brilliant, bluish-white, brittle metal, of specific gravity 6.715. It crystallizes in rhombohedrons, thus being isomorphous with arsenic and red phosphorus. Antimony melts at 450°, and may be distilled at a white heat. It tarnishes scarcely at all in the air, but takes fire at a red heat, producing antimonious oxide. It is strongly attacked by chlorine, forming antimonious and antimonic chlorides $SbCl_3$ and $SbCl_5$. The brittleness of antimony renders it useless in the metallic state, except for the construction of thermoelectric piles, where it is in conjunction with bismuth. Antimony is employed, however, to harden several useful alloys, such as type metal, shrapnel bullets, Britannia metal, pewter, etc.

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## COMPOUNDS OF ANTIMONY.

**102. Hydrogen Antimonide, or Stibine.**—Whenever an antimony compound is present in a solution from which hydrogen is being evolved, an inodorous gas escapes, mixed with the hydrogen, causing it to burn with a bluish-white flame. This gas is stibine $SbH_3$. It is analogous to arsine in its properties, and is similarly decomposed by heat; but the metallic deposit of antimony is easily distinguished from that of arsenic by its darker color, its smoky appearance, its less volatility, its insolubility in hypochlorites, and its solubility in ammonium sulphide.

**103. Antimonious and Antimonic Oxides and Acids.**—**Antimonic oxide** $Sb_2O_5$ is a yellowish, insoluble, and tasteless powder, of specific gravity 6.6. It is obtained by heating antimonic acid.

**Antimonic acid** is obtained by oxidizing antimony by nitric acid or by treating antimonic chloride with water. Both the ortho-acid $H_3SbO_4$ and the dimeta-acid $HSbO_3$ have also been obtained; and salts of diantimonic acid $H_4Sb_2O_7$ are also known.

**Antimonious Oxide** $Sb_2O_3$ occurs native, in two different crystalline forms, as *senarmontite* and *valentinite.* It is the product of the combustion of antimony in air, and is then crystalline; by pouring antimonious chloride into a boiling solution of sodium carbonate it is obtained as a dirty-white powder, which becomes yellow when heated. Antimonious acid $HSbO_2$ is a feeble acid, forming easily decomposable salts.

**104. Antimonic Sulphide.**—Antimonic sulphide $Sb_2S_5$ is obtained as a yellowish-red powder by the action of hydrogen sulphide on a solution of the chloride in tartaric acid, or by acidifying a solution of an alkaline sulphantimonate. It unites readily with sulphides of electropositive elements, forming sulphantimonates, having the general formula $M_3SbS_4$; of which sodium sulphantimonate $Na_3SbS_4,9Aq$—sometimes called *Schlippe's salt*—is an example.

**105. Antimonious Sulphide.**—Antimonious sulphide $Sb_2S_3$ has already been mentioned as one of the chief mineral sources of antimony, existing in nature as stibnite. It has a steel-gray color, a specific gravity of 4.5, and a strong metallic luster. It crystallizes in orthorhombic prisms. It is precipitated by hydrogen sulphide from antimonious solutions as a bright, orange-red body containing water, which becomes steel gray on fusion.

**106. Antimonious chloride** $SbCl_3$ and **antimonic chloride** $SbCl_5$ are formed when antimony is acted on by dry chlorine—the former, if the antimony is in excess; the latter, if the chlorine is in excess. Antimonic chloride may be readily formed by passing chlorine gas through the fused antimonious chloride.. Antimonious chloride is also obtained

by the distillation of an intimate mixture of the metal or its sulphide with corrosive sublimate $HgCl_2$.

As prepared by the above mentioned methods, the antimonious chloride is a crystalline mass. It melts at 73° and boils at 223°, but it is also frequently obtained as a viscous mass (known as *butter of antimony*) by dissolving the sulphide in concentrated hydrochloric acid and distilling the product. Antimonic chloride is a heavy, colorless, fuming liquid, from which crystals may be obtained by exposure to a freezing mixture of ice and salt.

Both chlorides are decomposed by water, forming oxychlorides, which are precipitated; prolonged treatment effects the removal of the whole chlorine, leaving (in the case of antimonious chloride) antimonious oxide $Sb_2O_3$, and (in the case of antimonic chloride) pyroantimonic acid $H_4Sb_2O_7$.

Antimony, like arsenic, forms a tri-fluoride, tri-bromide, and tri-iodide by the direct union of the elements. They are well crystallized substances, and by the action of the water form basic oxysalts.

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## VANADIUM.

*Symbol V. Atomic weight 51.2. Valence III and V.*

**107. Occurrence and Preparation.**—This element is found in a number of rather rare minerals, of which the most important is *vanadinite*, a double compound of chloride and vanadate of lead $3Pb_3(VO_4)_2, PbCl_2$. It is found in Scotland, Mexico, and Chile. Vanadic acid has also been found in some clays, in the cupriferous sandstone at Perm, in Russia, and Alderley Edge in Cheshire, England; it is also contained in some specimens of coal. By treating the vanadate of lead with nitric acid, expelling the excess of acid by evaporation, and washing out the lead nitrate with water, impure *vanadic anhydride* $V_2O_5$ is obtained, which may be purified by dissolving in ammonia, crystallizing the *ammonium metavanadate* $NH_4VO_3$, and decomposing it by heat, when vanadic

anhydride is left as a reddish-yellow, fusible solid, which crystallizes on cooling, and dissolves sparingly in water, giving a yellow solution. It dissolves in hydrochloric acid, and if the solution is treated with a reducing agent (such as hydrosulphuric acid) it assumes a fine blue color. If a solution of ammonium vanadate is mixed with tincture of galls, it gives an intensely black fluid, which forms an excellent ink, for it is not bleached by acids (which turn it blue), alkalies, or chlorine.

Vanadium itself has been obtained by heating its chloride in hydrogen, as a silver-white metal of specific gravity 5.5. It is neither oxidized by air at ordinary temperatures nor does it decompose water, but it burns when strongly heated in air. Its melting point has not yet been properly established. It is insoluble in $HCl$, but soluble in $HNO_3$. Fused $NaOH$ converts it into sodium vanadate.

**108. Compounds of Vanadium.**—The oxides of vanadium correspond in composition with those of nitrogen. $VO$ is a basic oxide forming salts which give lavender-colored solutions; these absorb oxygen rapidly from the air, and act as powerful reducing agents. $V_2O_3$ is a black, crystalline body, resembling plumbago, and is capable of conducting electricity; it is obtained by heating vanadic anhydride in a current of hydrogen; is insoluble in acids; and combines with bases to form vanadites $RVO_2$. $V_2O_4$ is produced when $V_2O_3$ is heated in air; it dissolves in acids, forming salts of *vanadyl* $VO$; and in alkalies, forming *hypovanadates* $R_2V_4O_9$. *Vanadic anhydride* $V_2O_5$ forms purple and green compounds with the above oxides. *Metavanadic acid* $HVO_3$ crystallizes in beautiful golden scales. The yellow fuming liquid, formerly called chloride of vanadium, is really an oxychloride, *vanadyl trichloride* $VOCl_3$. The *oxychlorides* $V_2O_2Cl$, $VOCl$, and $VOCl_2$ have also been obtained. There exist two compounds of vanadium with nitrogen, $VN$ and $VN_2$. Compounds of vanadium are now quite frequently used for blacks in calico printing, in conjunction with chlorates and aniline hydrochloride.

## NIOBIUM, OR COLUMBIUM, AND TANTALUM.

*Niobium: Symbol Nb, or Columbium: Symbol Cb. Atomic weight 94. Tantalum: Symbol Ta. Atomic weight 182.*

**109.** These elements are found closely associated in several minerals, and were, consequently, regarded as identical until 1846. Their principal sources are the minerals *columbite*, a niobate of iron and manganese $(NbO_3)_2FeMn$, in which more or less of the niobium is usually replaced by tantalum; *tantalite*, a ferrous tantalite $Fe(TaO_3)_2$, in which in like manner a portion of the tantalum is replaced by niobium; *pyrochlorite*, *yttrotantalite*, and *euxenite*, in which these elements are associated with *yttrium*, *cerium*, etc.

**110. Niobium.**—Niobium, also known as *columbium*, was obtained as steel-gray crusts by Roscoe, who passed through a red-hot tube the vapor of niobium chloride mixed with hydrogen. Niobium has a specific gravity of 7.06; it oxidizes with incandescence when heated in air, and burns, also, in chlorine.

There are three oxides of niobium, $Nb_2O_3$, $Nb_2O_4$, and $Nb_2O_5$. A mixture of the latter with the corresponding tantalic oxide may be obtained by fusing niobiferrous minerals with acid potassium sulphate, and boiling the fused mass with water. The residue is digested with ammonium sulphide, and the remaining powder boiled with hydrochloric acid. The two oxides, which are unaffected by this treatment, are then separated by converting them into *fluotantalate* and *fluoniobate of potassium;* the latter is much more soluble than the former. These potassium salts are then decomposed by boiling with sulphuric acid.

**111. Niobic Oxide.**—Niobic oxide $Nb_2O_5$ is a white, insoluble, and infusible powder, which takes a yellow color when heated, and which retains this color while hot. When strongly heated in hydrogen, it is reduced to the tetroxide $Nb_2O_4$, a bluish-black powder, which burns again to the pentoxide when heated to redness in air.

Niobic oxide is the anhydride of *niobic acid* $HNbO_3$, which

is obtained as a white powder by the reaction of *niobium pentachloride* $NbCl_5$ with water.

Niobium forms two chlorides, $NbCl_3$ and $NbCl_5$, as well as an oxychloride, $NbOCl_3$.

**112. Tantalum.**—Tantalum has probably not been obtained in a pure state. Berzelius obtained it as a black powder by heating potassium fluotantalate with potassium.

There are two oxides, $Ta_2O_4$ and $Ta_2O_5$. **Tantalic oxide** is separated from the niobic acid, with which it is associated in its minerals, by the process already indicated. It is a white, infusible powder, and becomes crystalline when heated. By strong ignition with charcoal it is converted into tantalous oxide.

**Tantalic acid** $HTaO_3$ is analogous to niobic acid, and forms, like this acid, a series of salts.

**Tantalum chloride** $TaCl_5$ is formed by heating an intimate mixture of tantalic oxide and charcoal in a current of chlorine.

**Niobic chloride** is formed in a similar manner. Both are fusible, volatile solids, crystallizing in yellow needles. There is no tantalum chloride corresponding to the niobous chloride $NbCl_3$.

## REVIEW OF THE BISMUTH GROUP OF METALS.

**113.** The metals *Bi*, *Sb*, *Ta*, *Nb*, and *V* belong to the same group of elements, which also includes *N*, *P*, and *As*. All these are characterized by their acid pentoxides. *Ta*, *Nb*, and *V* do not form hydrides analogous to $PH_3$, nor is $BiH_3$ known. Many points of resemblance may be noted between vanadium and chromium, while niobium and tantalum recall tungsten.

## TIN.

*Symbol Sn. Atomic weight 119. Valence II and IV. Molecular weight 238.*

**114. History and Occurrence.**—Tin has been known for many thousands of years; it is spoken of by Moses

(Numbers 31:22), and Homer mentions it in his Iliad. Much of the brass of the ancients was an alloy of copper and tin, the latter having been obtained from Cornwall, England, and Herodotus speaks of the British isles as the *tin islands*. The principal ore of tin is stannic oxide, known as the mineral *cassiterite*, or *tinstone*. It occurs in veins running through rocks—*vein* or *mine tin ores*—and also in the beds of streams, from the disintegration of these rocks—*stream-tin ores*. The principal localities of tin ore are Cornwall, England, and Banca and Malacca, India. It is also found, though less abundantly, in this country.

**115. Preparation.**—At the Cornish tinworks the purer portions of the ore are picked out by hand, and the residue, which contains quartz and other earthy impurities, together with copper pyrites and arsenical iron pyrites, is reduced to a coarse powder in the stamping mills, and washed in a stream of water. The tinstone, being extremely hard, is not reduced to so fine a powder as the pyritic minerals associated with it, and these latter are, consequently, much more rapidly carried away by the stream of water than the tinstone. The removal of the foreign matters from the ores is also much favored by the high specific gravity of the stannic oxide, which is 6.5, while that of sand or quartz is only 2.7, so that the latter would be carried off by a stream that would not disturb the former. So easily and completely can this separation be effected that sand containing less than 1 per cent. of tinstone is found capable of being economically treated.

In order to expel any arsenic and sulphur that may still remain in the washed ore, it is roasted in quantities of about 800 or 1,000 pounds in a reverberatory furnace, when the sulphur is disengaged in the form of sulphur dioxide and the arsenic in that of arsenious oxide, the iron being left in the state of ferric oxide, and the copper partly as sulphate of copper and partly as unaltered sulphide. To complete the oxidation of the insoluble sulphide of copper, and its conversion into the soluble sulphate, the roasted ore is moistened

with water and exposed to the air for some days, after which the whole of the copper may be removed by again washing with water.

A second washing in a stream of water also removes the ferric oxide in a state of suspension, and this is much more easily effected than when the iron is in the form of pyrites, since the difference between the specific gravity of this mineral (5) and that of the tinstone (6.5) is far less than that between the specific gravity of ferric oxide and tinstone.

The oxide thus purified contains between 60 and 70 per cent. of tin; it is mixed very intimately with about $\frac{1}{8}$ of powdered coal, and a little lime or fluorspar, to form a fusible slag with silicious impurities, and reduced in a reverberatory furnace—a comparatively easy task, since stannic oxide readily parts with its oxygen to carbon at red heat.

The tin-smelting furnace is shown in Fig. 3. The mixture of ore and coal is moistened to prevent its dispersion by the draft of air, and spread on the hearth *A* in charges of between 2,000 and 2,500 pounds. The temperature is not permitted to rise too high at first, lest a portion of the oxide of tin should combine with the silica to form a silicate, from which the metal would only be reduced with difficulty.

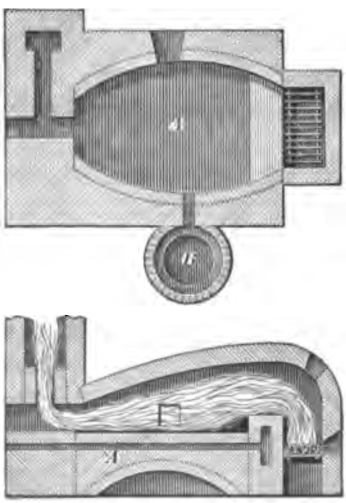

Fig. 3.

During the first 6 or 8 hours the doors of the furnace are kept shut, so as to exclude the air and favor the reducing action of the carbon on the stannic oxide, the oxygen of which it converts into carbonic oxide, leaving the tin in the metallic state to accumulate upon the hearth beneath the layer of slag. When the reduction is deemed

complete, the mass is well stirred with an iron paddle to separate the metal from the slag; the latter is run off first, and the tin is then drawn off into an iron pan *B*, where it is allowed to remain at rest for the dross to rise to the surface, and is ladled out into ingot molds.

The slags drawn out of the smelting furnace are carefully sorted—those containing much oxide of tin being worked up with the next charge of ore, while those in which globules of tin are disseminated are crushed, so that the metal may be separated by washing in a stream of water.

The tin, when first extracted from the ore, is, of course, far from pure, being always more or less contaminated with copper, arsenic, iron, and tungsten. In order to purify it, the ingots are piled into a hollow heap near the fire-bridge of a reverberatory furnace, and gradually heated to the fusing point, when the greater portion of the tin flows into an outer basin, while the remainder is converted into stannic oxide, which remains as dross upon the hearth, together with the oxides of iron, copper, and tungsten, the arsenic having passed off as arsenious oxide. Fresh ingots of tin are introduced at intervals, until about 5 tons of the metal have been collected in the basin, which is, as a rule, the case in about an hour after the beginning of the operation.

Owing to the low specific gravity of tin (7.29), any dross that may still remain mixed with it does not separate very readily; to obviate this, the molten metal is continually stirred for about 3 hours with wet wooden poles, when the evolved bubbles of steam carry the impurities up to the surface in a kind of a froth. The metal is then allowed to remain at rest for 2 hours, when it is skimmed and ladled into ingot molds. The tin thus obtained is commercially known as *block tin.* It has been observed that, owing to the lightness of the tin and its readiness to separate from its contaminating metals, the ingots cast from the metal first ladled out of the pot are purer than those obtained from the metal near the bottom; this is shown by striking the hot ingots with a hammer, when they break up into the irregular

prismatic fragments known as *drop* or *grain tin*, the impure metal not exhibiting this extreme brittleness at high temperature. The purest tin is imported from Banca, and is known as *Straits tin*.

**116. Properties.**—Tin is a brilliant-white metal and has a specific gravity of 7.29. It is dimorphous, crystallizing in forms belonging to the quadratic and isometric systems. It is quite malleable and may be beaten into very thin leaves; at 100° it is ductile and can be drawn into wire. Its tenacity is small. It crackles when a bar of it is bent, producing that peculiar noise known as the "cry of tin." It possesses a peculiar odor, and is a good conductor of heat and electricity. Its melting point is about 230°, and it distils at a white heat. Heated in air, it burns readily to oxide, though it retains its luster in air at ordinary temperature. It is readily attacked by acids.

**117. Uses.**—Tin is largely used in the arts for making tin foil, for plating iron in the manufacture of tin plate, and also as a constituent of many important and valuable alloys. With copper it forms gun metal, speculum metal, bell metal, and bronze; with lead it forms solder and pewter. Britannia metal is an alloy of tin, antimony, and copper. With mercury, tin yields an amalgam, which is used for producing the bright reflecting surface on glass mirrors.

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## COMPOUNDS OF TIN.

**118. Stannic Chloride.**—Stannic chloride $SnCl_4$, known to the alchemists in the middle ages as *liquor fumans Libavii*, may be obtained either by the direct action of chlorine gas on tin, or stannous chloride; or by distilling an excess of mercuric chloride with tin filings, according to the equation:

$$2HgCl_2 + Sn = 2Hg + SnCl_4$$

It is a colorless, fuming liquid, of specific gravity 2.28, which boils at 115°. Its vapor density is 130. It unites with

water readily, evolving heat, and forming crystalline hydrated chlorides containing varying quantities of water. $SnCl_4,3H_2O$, $SnCl_4,5H_2O$, and $SnCl_4,8H_2O$ are said to have been prepared in this way. With alkali chlorides it forms definite compounds, the potassium salt being $K_2SnCl_6$. It is used in dyeing.

**119. Stannous Chloride.**—Stannous chloride $SnCl_2$ may be prepared by distilling tin filings with the proper amount of mercuric chloride. It is a white or grayish mass, which has a greasy appearance and is nearly transparent. It melts at 250° and may be distilled at about 620°. By solution in water and evaporation, large, beautiful, prismatic crystals are produced, which have the composition $SnCl_2,2Aq$. These crystals are known as the *tin salt* of the dyer, for whose use they are usually manufactured by dissolving tin in hot concentrated hydrochloric acid.

The crystals of stannous chloride dissolve in a small quantity of water, forming a limpid liquid, but when treated with a large quantity of water, they yield a cloudy liquid, which holds in suspension a small quantity of white oxychloride. The atmospheric oxygen dissolved in water takes part in this decomposition of stannous chloride, from which it removes part of the metal, a corresponding quantity of stannic chloride being formed.

Stannous chloride reduces many oxygenized and chlorinated compounds, and is largely used in the laboratory. It decomposes the salts of silver and mercury, setting free the metal. It instantly decolorizes the purple solution of potassium permanganate.

**120. Stannic Oxide.**—Stannic oxide $SnO_2$ is found in nature as the mineral *cassiterite*, or *tinstone*, in the form of beautiful, hard, transparent crystals of a yellowish-brown color. It may be prepared by burning the metal in air or by igniting either of the hydrates. It is then obtained as a white powder, of specific gravity 6.6, which is insoluble in all acids except hydrofluoric acid. Owing to its hardness, it

is used for polishing glass, under the name of *putty powder*. When fused with alkali hydrates, it forms *stannates*.

**121. Stannic Acids.**—There exist two stannic acids, namely, *orthostannic acid* $H_4SnO_4$ and *metastannic acid* $H_2SnO_3$. Orthostannic acid is precipitated from alkaline stannates by acids, or from stannic chloride by ammonia, as a gelatinous mass, which loses water on drying in vacuo, and becomes metastannic acid. When tin is oxidized by nitric acid, a polymeric form of metastannic acid is produced, which, when dried at 100°, has the composition $H_{10}Sn_5O_{15}$. Sodium metastannate $Na_2SnO_3,3Aq$, made by fusing native tinstone with sodium hydrate, is used as a mordant in dyeing.

**122. Stannous Oxide.**—Stannous oxide $SnO$ is of little practical importance. It is obtained by heating stannous oxalate in a closed vessel. It is a black, crystalline powder, which is combustible in air. If water is added to $SnO$ a hydrate is formed, which gradually absorbs oxygen from the air, and passes into stannic acid. With sulphuric acid it forms stannous sulphate $SnSO_4$.

**123. Sulphides of Tin.**—Two sulphides of tin are known, namely, *stannous sulphide* $SnS$ and *stannic sulphide* $SnS_2$.

Stannous sulphide is obtained by heating tin filings with flowers of sulphur, but as this product still contains an excess of tin, the operation has to be repeated with a fresh quantity of sulphur. It is a lead-colored, crystalline mass. It is also produced as a dark-brown precipitate when a stannous solution is treated with hydrogen sulphide.

Stannic sulphide, also known as *bisulphide of tin*, is prepared by heating together tin amalgam, sulphur, and ammonium chloride. A golden-yellow, crystalline powder, having a specific gravity 4.6, a strongly metallic luster and greasy touch, is left in the vessel. The body has been known, for a long time, as *mosaic gold*. It is decomposed by red heat into stannous sulphide and sulphur. It is used as a bronze powder.

## TITANIUM.

*Symbol Ti. Atomic weight 48. Valence IV.*

**124. Occurrence and Preparation.**—Titanium exists in *rutile*, *brookite*, *edisonite*, and *anatase*, which constitute four varieties of titanic oxide $TiO_2$, and with iron in titaniferous iron ores. Cubical copper-colored crystals of a nitrocyanide of titanium or titanium cyanide and nitride are frequently found in the cinders of blast furnaces in which titaniferous ores have been reduced. These crystals are now believed to have the composition $Ti(CN)_2 3Ti_3N_2$.

Titanium is prepared by heating the double fluoride $K_2TiF_6$ in contact with metallic sodium or potassium, the alkaline fluorides formed being subsequently extracted with cold water. It is obtained as a black powder, which, on heating, unites directly with oxygen, chlorine, and nitrogen. Titanium is remarkable for its great affinity for nitrogen.

Titanium forms three chlorides, $TiCl_2$, $Ti_2Cl_6$, and $TiCl_4$; there are two well defined oxides, $Ti_2O_3$ and $TiO_2$, and possibly a third, $TiO$.

**125. Titanic Oxide.**—Titanic oxide $TiO_2$, mentioned in Art. **124**, occurs in different crystalline forms in nature; as square prisms in rutile, square octahedrons in anatase, and orthorhombic prisms in brookite. When prepared in a pure form from either of these minerals, it is a white, infusible, and insoluble powder. Like stannic oxide, it is the anhydride of an acid forming a well marked series of titanates.

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## ZIRCONIUM.

*Symbol Zr. Atomic weight 90. Valence IV.*

**126.** Zirconium resembles tin in its chemical relations. It is found in the rare minerals *zircon* and *hyacinth*, in which its oxide, *zirconia* $ZrO_2$, is combined with silica $ZrO_2,SiO_2$ or $ZrSiO_4$. Zirconia is obtained from these minerals by

heating with $KHF_2$, and boiling with water, when $K_2SiF_6$ is left and $K_2ZrF_6$ dissolved; this is heated with $H_2SO_4$ to expel $HF$, and $ZrO(OH)_2$ is precipitated by ammonia; when this is ignited, it incandesces, loses water, and becomes $ZrO_2$; this is a feebly acid oxide, liberating $CO_2$ from fused $Na_2CO_3$, and forming *sodium zirconate* $Na_4ZrO_4$.

Zirconium resembles silicon and is obtained like that element; it exists in an amorphous and a crystalline form. It dissolves in aqua regia and in hydrofluoric acid; it decomposes water slowly at 100°. Its melting point is very high. Zirconia is more basic than silica, and the metal displaces silicon when heated with silica. The sulphate of zirconium is decomposed by boiling with $K_2SO_4$. $ZrCl_4$ is also known, and is a more stable compound than $SiCl_4$. Evidence of the existence of higher oxides than $ZrO_2$ has been obtained.

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## THORIUM.

*Symbol Th. Atomic weight 231.5. Valence IV.*

**127.** Thorium was discovered by Berzelius in 1828, in the mineral *thorite*, found in Norway, and which is essentially a silicate of thorium, having the formula $ThSiO_4$.

Thorium is a dark-gray powder, obtained by heating, in the presence of metallic potassium, the chloride $ThCl_4$, or the double fluoride $2KF, ThF_4$. It closely resembles in its chemical properties titanium and zirconium. When strongly heated in air it burns brightly, forming the oxide $ThO_2$.

This oxide, usually called *thoria*, glows brightly at high temperatures and is largely used in association with *lanthana* $La_2O_3$ and other rare earths for the manufacture of the mantels used in the Welsbach light. A peroxide $Th_2O_7$ is obtained by precipitating solutions of thorium salts with ammonia in presence of hydrogen peroxide.

The other salts worth mention are the *tetrachloride* $ThCl_4$ and the *sulphate* $Th(SO_4)_2, 9H_2O$. The tetrachloride is prepared by heating an intimate mixture of the oxide with carbon in dry chlorine. It forms double salts with alkaline

chlorides, e. g., $ThCl_4,2KCl$, or $K_2ThCl_6$; and also with platinic chloride, $ThCl_4,PtCl_4,12H_2O$.

The sulphate likewise forms double salts with the alkaline sulphates, having the general composition $M_2SO_4,Th(SO_4)_2$.

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## GERMANIUM.

*Symbol Ge. Atomic weight 72.3. Valence IV.*

**128.** In 1886, Winkler discovered in the mineral *argyrodite*, which is a rare silver ore found near Freiberg, in Saxony, the element *germanium*. It is a grayish-white, lustrous metal; its melting point is about 900°, and it combines directly with chlorine, oxygen, and sulphur when heated with them. It forms two oxides, the lower oxide, $GeO$, of a dark color, the hydroxide of which is obtained by precipitating the bichloride $GeCl_2$ with potassium hydrate; and the higher oxide, $GeO_2$, by heating the metal in oxygen or with nitric acid. Its sulphides correspond with the oxides, having the formula $GeS$ and $GeS_2$, respectively. The latter forms sulphosalts by solution in alkaline sulphides. *Germanium tetrachloride* $GeCl_4$ is the most stable and most important of the compounds of germanium and chlorine; it is obtained by direct action of chlorine on the metal. It is a colorless, fuming liquid, and boils at 86°. The *bichloride* $GeCl_2$ is formed by heating the metal in hydrochloric-acid gas; it is a powerful bleaching and reducing agent, and by the action of water it yields an oxychloride $GeOCl_2$.

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## CERIUM.

*Symbol Ce. Atomic weight 140. Valence III and IV.*

**129.** Though this element resembles in many ways the metals of the aluminum group, it is now generally classed with the elements related to tin. It occurs chiefly in *cerite*, which is essentially a silicate of this metal. The mineral is decomposed by strong sulphuric acid, and the metals *Ce*, *La*, and *Di* are precipitated from the solutions as oxalates. The mixed oxides obtained by igniting this precipitate are

dissolved in nitric acid, and the solution, after removal of excess of acid by evaporation, poured into much water, whereupon basic cerium nitrate is precipitated.

The metal is prepared by electrolyzing cerous chloride. It is gray, ductile, and malleable; unchanged by dry air, but becomes iridescent in moist air; its specific gravity is 6.7, and its fusing point between that of *Sb* and *Ag*. Cerium may be kindled in air more easily than magnesium, and burns more brightly; it is soluble in dilute acids, and decomposes water very slowly.

Cerium forms two oxides, $Ce_2O_3$ and $CeO_2$; the first is the more basic, though $CeO_2$ does not appear to possess any acid properties. The cerous salts, corresponding with $Ce_2O_3$, are colorless and fairly stable, while the ceric salts, corresponding with $CeO_2$, are either yellow or red, and are readily reduced to cerous salts. Only one chloride, namely, *cerous chloride* $Ce_2Cl_6$ or $CeCl_3$, is known, but *ceric fluoride* $CeF_4$ has been prepared.

A red precipitate, stated to be a peroxide $CeO_3$, is formed when a cerous salt is heated with $NH_3$ and $H_2O_2$.

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## LEAD.

*Symbol Pb. Atomic weight 206.4. Valence II and IV. Specific gravity 11.37.*

**130. History and Occurrence.**—Lead is one of those metals that have been known from the earliest ages of history. It is frequently mentioned in the Old Testament and other sacred writings. The Romans worked the lead ores of Spain and of England, and the Carthagenians those of Spain, the extent of their mining and smelting operations exciting surprise, even at the present day. The principal workable ore of lead is its sulphide, *galenite*, or more popularly known as *galena*, though it occurs also somewhat abundantly as *carbonate*, or *cerussite;* as *sulphate*, or *anglesite;* as *chloro-arsenate*, or *mimetite;* as *chlorophosphate*, or *pyromorphite*, and in sundry other forms.

**131. Preparation.**—The preparation of lead is a comparatively simple metallurgical process, and we shall only deal, in this course, with the methods employed in its extraction from galena, which may be considered as the chief source of this metal. For the richer ores the first part of the process is carried on in a reverberatory furnace at a moderate temperature, whereby part of the galena is converted into oxide and sulphate:

$$(1)\quad 2PbS + 3O_2 = 2PbO + 2SO_2$$

$$(2)\quad PbS + 2O_2 = PbSO_4$$

The temperature is then raised and the remaining sulphide reacts by double decomposition with the oxide and sulphate formed in the first stage:

$$(3)\quad PbS + 2PbO = 3Pb + SO_2$$

$$(4)\quad PbS + PbSO_4 = 2Pb + 2SO_2$$

With the exception of about 10 per cent., which remains in the slags, the lead is thus obtained in the metallic condition. After running off the lead, the residue in the slags is extracted by adding lime and a little coal, and submitting the mixture to further heating. The poorer ores are usually treated in a small blast furnace or cupola, and this method may be employed for the working of slags. In this case iron or ferrous silicate is the active agent in the removal of sulphur, and the lead obtained contains considerable quantities of silver, copper, antimony, and other metals. Such a process is in use in Germany, at Clausthal and Freiberg.

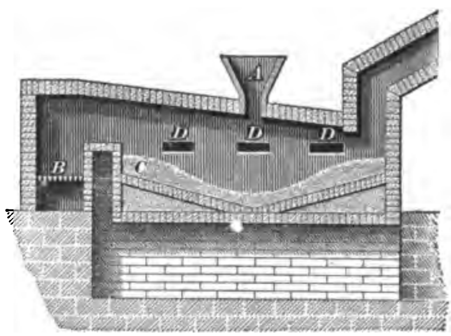

FIG. 4.

For working the richer ores a reverberatory furnace, as shown in Fig. 4, is employed. The essential elements in the construction of such a furnace are, as shown in the figure: the hopper $A$, at which the

charge is introduced; the fireplace *B*, at one end and separated from the hearth by a rather high fire-bridge; the hearth *C*, formed by molding slag in the form shown, the depression serving for the collection of the molten lead, and the slopes of the hearth for the spreading of the charge so as to expose it to the action of the fire gases and for working the slags; the doors *D*, *D*, *D* for regulating the supply of air and working the charge.

The first part of the process is carried out at dull red heat, and is essentially one of calcination and oxidation, during which reactions (1) and (2) take place. The doors are then closed and the temperature raised to a full red heat, when reactions (3) and (4) are effected.

Another form of furnace, known as the *Scotch hearth*, largely used in the northern parts of England, differs essentially from the above in that the hearth is shallow and that a blast is provided. The success of the process depends on the proper admixture of the fresh ore with that which has undergone oxidation, and in the regulation of the supply of air and fuel. The changes consist partly in those described previously; viz., the oxidation of part of the ore and the double decomposition that takes place between this and the fresh ore, and partly in reduction by the fuel added. Fig. 5 shows in section the form of hearth used in Scotland and the northern parts of England; the essential parts being: the hearth *A*, about 4 to 6 inches deep; the work stone *B*, provided with a shallow rim and a diagonal groove for running off the lead; the pot *C* for the reception of the

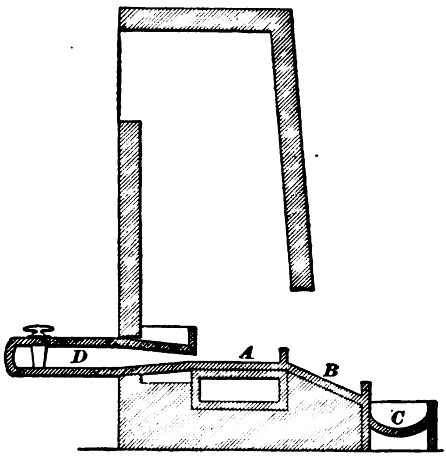

FIG. 5.

metal; the tuyere *D*, at the back of the hearth, for providing the blast.

Slags are usually worked up separately in a furnace of a similar type, but having a shaft above the hearth some 3 feet high, in which the slag and fuel are placed as in a blast furnace.

The lead obtained by any of these processes frequently contains sufficient antimony, besides tin, copper, iron, silver, etc. to render it hard, and it is in this case submitted to a process of *softening*. The metal is heated on the bed of a reverberatory furnace until the antimony, copper, etc. become oxidized and form a scum on the surface. This is skimmed off along with litharge which collects with it, and the process continued until the lead shows the proper degree of softness.

**132. Desilverizing Lead.**—As lead frequently contains silver in sufficient quantities to make it worth recovering, a number of processes have been invented for this purpose. Among these, those of Pattinson, Rozan, and Parkes are the best known.

The *Pattinson process* depends on the fact that pure lead solidifies at a somewhat higher temperature than an alloy of silver and lead. When lead containing silver is melted, as it cools the purer lead crystallizes out first, and if this is removed by a perforated ladle, the liquid remaining is richer in silver. By repeating this treatment the silver accumulates, until a ton of the lead contains as much as 600 to 700 ounces of silver, after which the silver is best separated by *cupellation*.

The *Rozan process* is similar in principle, but the proper temperature is attained by the use of high-pressure steam and cooling by water. Much larger quantities can be acted on at the same time, and there is the further advantage that the extreme agitation and contact with air promotes the removal of antimony and other impurities at the same time.

In the *Parkes process*, zinc is added to the metal in suitable proportions, an alloy of lead, zinc, and silver in this

case solidifying, while the lead free from silver remains molten.

**133. Cupellation.**—For obtaining the silver free from lead the metal is heated in an oxidizing atmosphere on a *cupel*, i. e., in a special furnace, the bed of which is made of bone ash impregnated with pearlash. The lead is oxidized to litharge, which collects at the surface of the charge and is blown off or to some extent absorbed by the bed of the furnace, carrying with it the impurities and leaving molten silver.

**134. Properties.**—Lead is a soft, brilliant, bluish-white metal. It leaves upon paper a bluish-gray streak, and is very malleable. It has a specific gravity of 11.37, crystallizes in regular octahedrons, and fuses at 325°. At a white heat it may be distilled. It has but a feeble tenacity, a wire 2 millimeters in diameter sustaining only a weight of 9 kilograms. Its freshly cut surface tarnishes in ordinary air, but remains bright in perfectly dry air and also in water free from air. Potable waters in general act on lead, dissolving it, and partly precipitating it as carbonate. This action is particularly noticeable in well waters that contain nitrates from decomposed animal matter, or chlorides from saline infiltration. Lead water pipes should, therefore, be avoided as a rule. When melted in the air, lead is rapidly converted into the oxide. It is scarcely attacked by sulphuric or hydrochloric acid at ordinary temperature, but dissolves readily in nitric acid. In presence of air and moisture it is acted on by quite feeble acids, such as acetic and carbonic acids. Hence, the use of vessels made of lead or soldered with lead should be avoided for cooking vegetables, fruit, etc., which all contain more or less acid.

Lead, when taken into the system, unites definitely with certain tissues and is retained there, until finally sufficient of it accumulates to produce poisoning. Acute colic is characteristic of poisoning by a large dose of lead, but in chronic poisoning, which is far more common, there is paralysis, particularly in the muscles of the forearm, causing

the wrist to drop; or there may be simply an indefinable feeling of malaise, accompanied by dyspeptic symptoms.

**135. Uses of Lead.**—This metal is largely used in the manufacture of pipes for the distribution of water and gas, and, mixed with a small portion of arsenic, in the manufacture of shot. When reduced to sheets, it is made into gutters, the covering of roofs, and linings for troughs and reservoirs. Alloyed with antimony and tin, it forms type metal; with bismuth, the soft alloy used for permanent pencil points; with tin, it makes pewter and soft solder; and with tin, cadmium, and bismuth, the fusible metal that melts at 60° to 65°.

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## COMPOUNDS OF LEAD.

**136. Plumbic Oxide.**—Plumbic oxide $Pb''O$ occurs native as the mineral *massicot*. It is prepared on a large scale in the arts under the name of *litharge*, by heating melted lead in a current of air. Its color is either pale yellow or orange yellow, according to the temperature at which it is prepared. It is dimorphous, crystallizing in rhombic octahedrons and in regular dodecahedrons. It fuses at red heat. Its specific gravity is 9.42. Acids dissolve it very readily, forming definite salts. It is only difficultly soluble in water, 7,000 parts of water being required to dissolve 1 part of plumbic oxide. It is soluble in alkali-hydrate solutions, as well as in lime water. Litharge is employed in the manufacture of glass, of lead acetate, and of white lead. It gives drying properties to linseed oil.

**137. Plumbic Hydrate.**—When a solution of lead is treated with an alkaline hydrate, a white precipitate is obtained, the composition of which does not appear to be firmly established. Some chemists regard this as the hydrate $Pb(OH)_2$, while others consider it an oxyhydrate $Pb_2O(OH)_2$, and claim the hydrate $Pb(OH)_2$ is only obtained in dilute solution as a sweetish alkaline liquid, by the action of pure water on $PbO$.

**138. Plumbic Peroxide.**—Plumbic peroxide $Pb^{iv}O_2$ is obtained as a brown powder by treating *minium*, or *red lead*, with dilute nitric acid, and washing the precipitate with boiling water. Plumbic peroxide is insoluble in water; it is readily decomposed by heat, losing half its oxygen and being converted into plumbic oxide. It is an energetic oxidizing agent. When it is briskly triturated with sulphur, the latter is inflamed.

If plumbic peroxide is introduced into a test tube with sulphurous oxide, the latter is immediately absorbed, with formation of lead sulphate:

$$SO_2 + PbO_2 = PbSO_4$$

Digested with ammonium hydrate it forms water and lead nitrate; it sets iodine free from potassium iodide, and bleaches a solution of sulphindigotic acid.

Plumbic peroxide combines directly with the oxides of potassium, sodium, calcium, and even lead, forming salts called plumbates, having the general formula $M_2PbO_3$. *Potassium plumbate* occurs in white octahedrons decomposable by water. Plumbic plumbates form the various compounds known as *red leads*. The compound $Pb_2''Pb^{iv}O_4$ (*plumbic orthoplumbate*), more frequently written $Pb_3O_4$, occurs as minium. This, as well as *plumbic metaplumbate* $Pb''Pb^{iv}O_3$ or $Pb_2O_3$, is produced largely in the arts as a pigment, by oxidizing litharge in a current of air, and then cooling very slowly.

**139. Plumbous Oxide.**—When lead oxalate $PbC_2O_4$ is heated to 300° in a closed vessel, a black, velvety powder is obtained, which is plumbous oxide $Pb_2O$. Though it contains neither metallic lead nor plumbic oxide, it takes fire when heated in air, producing this oxide.

**140. Lead Sulphide.**—Lead sulphide $PbS$ occurs as *galena* in nature in beautiful cubical crystals of a bluish-gray color and a metallic luster; its specific gravity is 7.58. It melts at red heat. When heated in contact with air, it is converted into oxide and sulphate, and, by the reaction of an excess of sulphide on these compounds, metallic lead is

produced. Hot, fuming nitric acid converts lead sulphide into sulphate. Concentrated and boiling hydrochloric acid transforms it into chloride, with evolution of hydrogen sulphide.

Galena is used for glazing common pottery. A broth of powdered galena and cow's dung mixed with water is applied to the surface of the previously well dried vessels.

This sort of pottery is generally baked at a temperature not very high, so that the sulphide of lead, the oxidation of which is prevented by the cow's dung, melts and spreads over the surface, forming a varnish of a dark color when cold. Nevertheless, a small quantity of oxide is always formed by the oxidation of the galena. When the baking takes place at a higher temperature, this oxide forms a fusible silicate, which covers the pottery. This glazing frequently has a green color, due to the presence of oxide of copper, and is attacked by vinegar and other acids, which dissolve the oxides of lead and copper. Hence, the danger in the use of ware so glazed for culinary purposes.

**141. Plumbic Chloride.**—Plumbic chloride $Pb''Cl_2$ has been found in the crater of Vesuvius after an eruption and is known as *cotunnite.* It is precipitated from any plumbic solution, if sufficiently concentrated, upon the addition of hydrochloric acid or a soluble chloride. It is a heavy, white powder, soluble in 135 parts of cold and 30 parts of boiling water, from which it crystallizes, on cooling, in lustrous needles. It melts when heated in closed vessels, and sublimes at a higher temperature. The fused chloride is translucent and sectile, and is known as *horn lead.* White and yellow oxychlorides are used as pigments, variously known as *mineral yellow*, *Turner's yellow*, and *Cassel yellow.*

**142. Plumbic Perchloride.**—Plumbic perchloride $Pb^{iv}Cl_4$ is obtained in solution by dissolving plumbic peroxide in cold hydrochloric acid, and in crystals by evaporating this solution in vacuo. It is a compound of which comparatively little is known.

**143. Lead Iodide.**—Lead iodide $PbI_2$ is obtained as a beautiful yellow precipitate when a solution of potassium iodide is added to a solution of lead acetate. This compound melts to a red-brown liquid at a high temperature. Lead iodide is soluble in 1,235 parts of cold and 194 parts of boiling water. On the cooling of its saturated, boiling solution, it is deposited in golden-yellow, hexagonal scales having a magnificent luster.

**144. Lead Nitrate.**—Lead nitrate $Pb(NO_3)_2$ is prepared by dissolving litharge in dilute nitric acid, from which it crystallizes in white, regular octahedrons. The crystals decrepitate when they are heated; they dissolve in 7½ times their weight of cold water, and in a much less quantity of boiling water.

At a red heat this salt is decomposed into nitrogen peroxide, oxygen, and plumbic oxide.

**145. Lead Sulphate.**—Lead sulphate $PbSO_4$ is one of the most insoluble of the lead salts; it dissolves readily in caustic alkalies, and slightly in moderately concentrated sulphuric acid, separating out again when the acid is largely diluted.

**146. Lead Carbonate.**—Lead carbonate $PbCO_3$, or basic carbonates of variable composition, are precipitated when sodium carbonate is added to a solution of lead nitrate. The basic carbonate known as *white lead* is of great importance, in consequence of its application as a white pigment. If a solution of lead acetate is boiled with lead oxide and then filtered, a basic acetate is obtained, and on passing carbon dioxide through the solution a white precipitate of basic carbonate, essentially $(PbCO_3)_2, Pb(OH)_2$, is deposited.

Prepared in this way, however, the pigment is denser and does not possess the same covering power as that formed more gradually by the so called *Dutch process*. In this

process, coils of sheet lead are placed in conical vessels, as shown in Fig. 6, resting on a ledge, the bottom of the vessel containing weak acetic acid. These vessels are about 8 inches high, and a large number are stacked together in layers, each layer being covered with tan or other fermenting vegetable matter. The stacks are very large, say 15 feet square by 20 feet high, and the heat generated by the fermentation gradually volatilizes the acetic acid and brings it into contact with the lead, and at the same time the carbon dioxide formed during the fermentation reacts with the basic acetate, yielding the basic lead carbonate. The acetic acid is then free to act on a further portion of lead, and the process repeats itself until practically the whole of the lead is transformed into *white lead.*

FIG. 6.

**147. Lead Chromate.**—Lead chromate $PbCrO_4$ is found crystallized in nature, constituting the mineral *crocoite* found in Siberia. It may be prepared by double decomposition between solutions of potassium chromate and lead acetate; a yellow precipitate is thus obtained, and is employed in painting, etc. under the name of *chrome yellow.*

Lead chromate melts at a red heat; at a white heat it loses 4 per cent. of oxygen. It is easily reduced by charcoal and hydrogen. Insoluble in water, it dissolves readily in solutions of potassium hydrate.

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## REVIEW OF THE TIN GROUP OF METALS.

**148.** This group comprises *Ti*, *Zr*, *Ce*, *Th*, *Ge*, *Sn*, and *Pb*. These metals belong to a group of elements that include *C* and *Si*, the higher salt-forming oxide being $RO_2$, which in most cases behaves as a feeble acid oxide, resembling $CO_2$ and $SiO_2$.

## THALLIUM.

*Symbol Tl. Atomic weight 203.6. Valence I and III.*

**149. History and Occurrence.**—Thallium was discovered in 1861, by Crookes, in seleniferous flue dust from sulphuric-acid works in the Harz Mountains in Germany. The residue colored a gas flame intensely green, and gave a spectrum consisting of one brilliant green line. From the characteristic tint of this line, Crookes named the metal *thallium*, which is derived from the Greek *θαλλός*, *thallos*, meaning "green," or "young shoot." Thallium was independently discovered by Lamy nearly a year later.

Thallium is widely distributed in nature, but constitutes only a very small proportion of the minerals in which it occurs, excepting in the very rare mineral *crookesite*, which contains from 16 to 18 per cent. of this metal.

**150. Preparation and Properties.**—Thallium is generally obtained from the dust deposited in the tubes that in sulphuric-acid works convey the sulphurous oxide from the pyrite burners to the leaden chambers. This is extracted with water, and the thallium is precipitated from this solution as chloride. This, by solution in sulphuric acid, gives the sulphate; and from this, metallic thallium may be precipitated by zinc.

The metal is of a bluish-white tint, and has, at the freshly cut surface, a silver-like luster, and bears generally a very great resemblance to lead. It has a specific gravity of 11.8. Owing to the want of tenacity, it is malleable, but not ductile. It melts at 294° and crystallizes in octahedrons. It tarnishes rapidly in the air, and burns brilliantly in oxygen. Nitric acid dissolves it readily. It forms two series of salts—the *thallous*, in which thallium is monovalent, and replaces the hydrogen of the acid, atom for atom; and the *thallic*, in which 1 atom of this metal replaces 3 atoms of hydrogen.

## COMPOUNDS OF THALLIUM.

**151. Thallous Oxide.**—Thallous oxide $Tl_2O$ is a black powder obtained by heating the hydroxide $TlOH$ in a steam bath in such a manner as to avoid its becoming further oxidized.

The hydroxide may be prepared in solution by exposing the metal to the action of air and water, or by adding baryta water to a solution of the sulphate:

$$Tl_2SO_4 + Ba(OH)_2 = BaSO_4 + 2TlOH$$

From a concentrated solution, crystals having the composition $TlOH, 2Aq$ are deposited.

**152. Thallic Oxide.**—Thallic oxide $Tl_2O_3$ is prepared by burning the metal in oxygen. If, to a solution of thallous chloride $TlCl$, sodium hypochlorite is added, a brown precipitate is obtained, which appears to be *thallic hydroxide* $Tl(OH)_3$.

**153. Thallic and Thallous Sulphide.**—Hydrogen sulphide does not afford a precipitate in thallium solutions in the presence of inorganic acids,* but in the neutral or alkaline solution of a thallous salt, or in presence of acetic acid, *thallous sulphide* $Tl_2S$ is precipitated. *Thallic sulphide* $Tl_2S_3$ is formed as a black mass by heating the metal with excess of sulphur.

Like the alkalies, thallium forms a *thallous fluoride* $TlF$, and a *thallous hydrofluoride* $TlHF_2$, the method by which these salts are prepared being also similar.

**154. Thallous Chloride.**—Thallous chloride $TlCl$ is formed by burning thallium in chlorine or by precipitating a solution of a thallous salt with hydrochloric acid. This is a white, curdy precipitate, which, like silver chloride, turns

* The name mineral acids is frequently applied in textbooks to those acids (i. e., sulphuric, hydrochloric, and nitric acids, etc.) which are here termed "inorganic acids."

to a violet color on exposure to sunlight; and, like lead chloride, is only very slightly soluble in cold, but reasonably soluble in boiling water. If thallous chloride is suspended in water through which a stream of chlorine gas is passed, *thallic chloride* $TlCl_3$ is obtained.

*Bromides* and *iodides* having a similar composition to the chlorides have also been prepared. They are even less soluble than the chlorides.

*Thallous chlorate* $TlClO_3$ and *thallous perchlorate* $TlClO_4$ are salts that closely resemble the corresponding potassium salts.

**155. Thallous Sulphate.**—Thallous sulphate $Tl_2SO_4$ is formed by the action of sulphuric acid on either metallic thallium or on thallium salts. It is isomorphous with potassium sulphate, and like it forms an alum $Tl_2SO_4, Al_2(SO_4)_3, 24Aq$, and double salts with the sulphates of magnesium, iron, and nickel of the general composition $Tl_2SO_4, RSO_4, 6H_2O$ ($R$ being either of the three metals mentioned). In presence of excess of sulphuric acid, *thallium hydrosulphate* $TlHSO_4$ is formed. By the action of sulphuric acid on thallic oxide, *thallic sulphate* $Tl_2(SO_4)_3$ is obtained.

**156.** *Thallous carbonate* $Tl_2CO_3$ as well as *thallous* and *thallic nitrates* and *phosphates* are also known.

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## COPPER.

*Symbol Cu. Atomic weight 63. Valence I and II.*

**157. History and Occurrence.**—Copper has been known from the earliest times. The Romans obtained it from the island of Cyprus and called it *aes Cyprium*, a term that afterward became *cuprum*, from which the English word *copper* is derived. Copper is found abundantly in nature, both free and in combination. Native copper occurs in masses of great size near Keweenaw Point, Lake Superior;

in Cornwall, England; in Siberia and the Ural Mountains, Russia. As cuprous oxide $Cu_2O$ in the mineral *cuprite*, it is found in Cornwall, England, South America, and Australia; as cuprous sulphide $Cu_2S$ in *copper glance*, and associated with sulphide of iron in *copper pyrites;* as basic carbonate in *malachite* $CuCO_3, Cu(OH)_2$, and in *azurite* $2CuCO_3, Cu(OH)_2$. In addition to these minerals, which are used for the extraction of copper on a large scale, mineral silicates, phosphates, arsenates, and oxychloride are known. Copper is also found in the coloring matter of the red wing feathers of certain birds.

**158. Preparation.**—The method applied for the extraction of copper naturally varies with the ore under treatment. The oxides and carbonates are simply heated with charcoal or other fuel, with the addition of some silicious flux. The process of extracting copper from a mixture of copper sulphides and oxidized ore is a more complex operation, and a rather interesting one from a chemical point of view. It will be outlined here, describing, first, the chemical reactions involved, and then the essential operations by which metallic copper is ultimately obtained.

**Chemical Reactions.**—Copper possesses a great affinity for sulphur and a smaller affinity for oxygen than the metals (especially iron) with which it is associated.

1. The ore is first moderately heated, when part of the sulphur and arsenic are oxidized, and pass off as sulphur dioxide and arsenic trioxide, respectively. This operation is regulated so that part of the sulphur is retained in the form of cuprous sulphide $Cu_2S$, the iron and part of the copper being transformed into oxide. The charge is then brought to a fusion at a higher temperature, when the ferrous oxide enters into combination with the silica, either originally contained in the ore or added to the charge, to form a slag of ferrous silicate. By a repetition of roastings and fusions the iron is thus ultimately removed.

2. At a moderate temperature the cuprous sulphide is then partially oxidized, and the temperature is raised

so that the cuprous oxide formed may react with the sulphide:

$$2CuO + Cu_2S = 4Cu + SO_2$$

The remainder of the sulphur is thus eliminated and metallic copper obtained. Any sulphide of iron that still remains is also acted on by the cuprous oxide as follows:

$$3CuO + FeS = 3Cu + FeO + SO_2$$

3. The crude copper so obtained is further refined by a process that is described below.

**159. The Actual Operations.**—1. *Calcination.*—This is performed either in heaps or on the bed of a reverberatory furnace. In the former the ore is made into heaps, the height of which varies according to the richness of the ore, being for rich ore about 5 feet, and for poor ore about 7 feet. The heat requisite is obtained by the firing of logs of wood placed in a layer in the lower part of the heap, vents

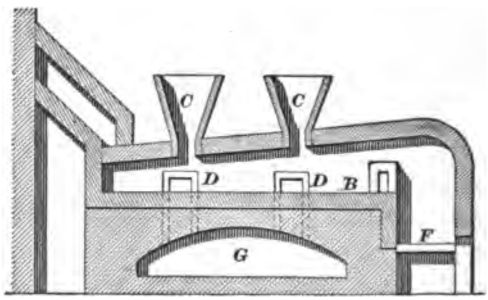


FIG. 7.

being provided so that a sufficient supply of air may be brought in contact with the ore. The main objects of this calcination are the removal of part of the sulphur and the volatilization, as completely as possible, of any arsenic or antimony present in the ore, as these substances are most prejudicial to metallic copper. If the calcination is carried out in a reverberatory furnace (Figs. 7 and 8), the chief provisions to be attended to are a low temperature (secured

by having the fire-grate *F* small in proportion to the bed of the furnace *B*, viz., 1 to 15 or 20), and a properly regulated air supply admitted at *A*. The charge is introduced at the hoppers *C*, and spread over the bed of the furnace, being worked from the doors *D*, and finally withdrawn through openings *E* in the bed of the furnace, and shot down into the vault *G*, the course of the discharge exits being shown by dotted lines in Fig. 7.

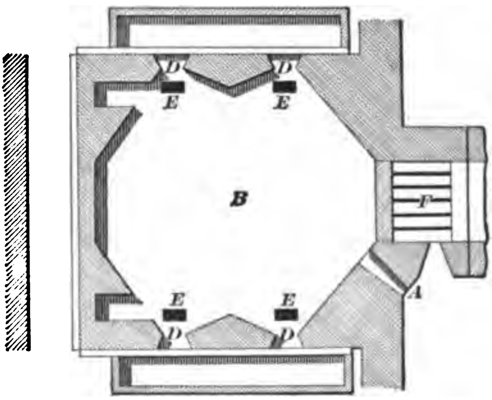


FIG. 8.

2. *The Fusion.*—A higher temperature is required for this process, which is carried out in a reverberatory furnace somewhat like the one shown in Figs. 7 and 8, but whose grate area in proportion to the furnace bed is considerably larger, about 1 to 5. At this stage ferrous oxide forms by double decomposition between ferrous sulphide and cuprous oxide, and this combines with silica, forming the slag and ferrous and lime silicate, while the cuprous sulphide and the ferrous sulphide still remaining, form the *regulus*, or *coarse metal.* The slag contains only very little copper and is run off and thrown away, as it would hardly pay the expense if an attempt were made to extract what little copper it does contain. The regulus contains cuprous and ferrous sulphide in about equal proportions.

3. The regulus is brought into a fine state of division by

running, while still hot, from the furnace into water. The calcining and fusing operations, previously described, are repeated several times in order to remove the iron as completely as possible. The product thus obtained is known as *white metal*, and consists essentially of cuprous sulphide.

4. *The Roasting.*—The object of this operation is to partially oxidize the cuprous sulphide and induce the rest of the iron and other impurities, that may be still contained in the white metal, to form a slag. This operation is performed in a reverberatory furnace whose fire-grate is still smaller than that of the furnace used in the calcining process, and with an increased supply of air. When the oxidation has proceeded far enough, the temperature is raised so as to bring about the reaction between the cuprous oxide and the sulphide.

5. *The Refining.*—The crude copper, technically known as *blister copper*, is fused in an oxidizing atmosphere on the bed of the refining furnace, and the still remaining impurities, such as arsenic, iron, antimony, sulphur, etc., are oxidized and skimmed off as slag. Finally, anthracite is sprinkled on the surface of the molten metal and the mass stirred with the trunk of a young tree—a process known as *poling*. In this way the reduction of any remaining cuprous oxide is effected, and particles of slag are carried to the surface.

Another method of obtaining copper is its extraction from burned pyrites. Much of the pyrites now used in the manufacture of sulphuric acid contains considerable copper, and to extract this the burned pyrites is ground and intimately mixed with from 10 to 20 per cent. of its weight of salt, and then roasted in a reverberatory furnace, so as to obtain the iron as far as possible in the form of ferric oxide, the copper being left chiefly as cupric chloride. The product is then lixiviated with water to extract the copper salts, and deposition effected by means of scrap iron.

Perfectly pure copper is also obtained in this country by an electrolytical process.

**160. Properties.**—Copper is a lustrous, sonorous metal of a flesh-red color. Its specific gravity is about 8.9, and it is somewhat softer than iron. When rubbed with the hand it gives off a peculiar, disagreeable odor. It crystallizes in isometric forms, and conducts heat and electricity very readily. It may be drawn into fine wire or beaten into thin leaves. Its tenacity is considerable, being next to iron. A copper wire 2 millimeters in diameter sustains a weight of 140 kilograms. It melts at 1,054° and may be volatilized by the heat of the oxyhydrogen blowpipe. It is unaltered in dry air at ordinary temperatures, but it absorbs oxygen in the presence of moisture and carbon dioxide. Green spots then appear upon its surface, constituting a carbonate of copper. At a high temperature copper absorbs oxygen very eagerly, being converted into black, cupric oxide, if the oxygen is in excess; or in red, cuprous oxide, if the metal is in excess. The oxidation of copper is accelerated if the metal is in a state of fine division; in fact, when very finely powdered it often takes fire spontaneously. Weak acids, alkalies, and saline solutions act on it slowly in the presence of air; hence, as all its salts are more or less poisonous, anything to be taken as food should not be prepared in vessels made of copper or any of its alloys.

Copper is much employed for the construction of boilers, stills, and worms. Owing to its high electric conductivity, enormous quantities of it are used in electric construction for cables, dynamos, etc. Sheet copper is used for coating the bottoms of ships, for roofing, etc.

**161. Alloys of Copper.**—Copper forms a greater number of alloys than any other metal. Those of copper with tin (gun metal and bronze) have already been mentioned in Art. **117**. With from one-third to one-half its weight of zinc, copper forms *brass*, which is much harder than copper, and capable of being hammered into thin leaves and used as a substitute for gold. The most important alloys of which copper is a predominant constituent are given in Table 3.

**TABLE 8.**

| Alloys. | Copper. | Other Constituents. |
|---|---|---|
| Brass. | 64 parts | 36 parts zinc. |
| Muntz's metal. | 60 to 64 parts | 40 to 36 parts zinc. |
| German silver. | 61 parts | 19.5 parts zinc, 19.5 parts nickel. |
| Aich's or Gedge's metal | 60 parts | 38.2 parts zinc, 1.8 parts iron. |
| Sterro metal | 55 parts | 42.4 parts zinc, 2.6 parts iron. |
| Bell metal | 78 parts | 22 parts tin. |
| Speculum metal. | 66.6 parts | 33.4 parts tin. |
| Bronze | 85 parts | 10 parts tin, 5 parts zinc. |
| Gun metal. | 90.5 parts | 9.5 parts tin. |
| Bronze coinage. | 95 parts | 1 part zinc, 4 parts tin. |
| Aluminum bronze. | 90 parts | 10 parts aluminum. |

**162. Brass.**—Brass is made by melting copper, and adding rather more than half its weight of zinc. An alloy containing 32 per cent. of copper and 68 per cent. of zinc would correspond with the formula $Zn_2Cu$, which is the only compound of $Cu$ with $Zn$ that has been isolated; thus, ordinary brass may be regarded as a solidified solution of this compound in copper. A small quantity of tin is added to brass intended for door plates, making the engraving of them much easier. When it has to be turned or filed, about 2 per cent. of lead is usually added to it, in order to prevent adhering to the tools used. Brass cannot be melted without losing a portion of its zinc in the form of vapor. When exposed to frequent vibration (as, for instance, in the suspending chains of chandeliers) it undergoes an alteration in structure and becomes extremely brittle. The solder used by braziers consists of equal weights of copper and zinc. In order to prevent ornamental brasswork from being tarnished by the action of air, it is either lacquered or bronzed.

*Lacquering* consists simply in varnishing the brass with a solution of shellac in spirit, colored with a resin known as dragon's blood. *Bronzing* is effected by applying a solution of either arsenic, mercury, or platinum to the surface of the brass. By the action of arsenious oxide dissolved in hydrochloric acid, on brass, the latter acquires a coating composed of arsenic and copper, which imparts a bronzed appearance, the zinc being dissolved in place of the arsenic, which combines with the copper of the surface. A mixture of corrosive sublimate (mercuric chloride $HgCl_2$) and acetic acid is also sometimes employed, when the mercury is displaced by the zinc and precipitated upon the surface of the brass, with which it forms a bronze-like amalgam. For bronzing brass instruments, such as theodolites, levels, etc., a solution of chloride of platinum is employed, the zinc of the brass precipitating a very durable film of metallic platinum upon its surface.

$$PtCl_4 + Zn_2 = Pt + 2ZnCl_2$$

## COMPOUNDS OF COPPER.

**163. Cuprous Oxide.**—Cuprous oxide $Cu_2O$ is found in nature in either vitreous masses or red octahedral crystals.

It is ordinarily prepared in the wet way by boiling a solution of copper sulphate in an excess of potassium hydrate with glucose; a bright-red, crystalline powder is precipitated, which is anhydrous cuprous oxide. When heated in contact with air, it absorbs oxygen and is converted into cupric oxide.

When potassium hydrate is added to a solution of cuprous chloride, a yellow precipitate of cuprous hydrate is thrown down. Cuprous oxide is used to communicate a red color to glass.

**164. Cupric Oxide.**—Cupric oxide $CuO$ occurs native as the mineral *melaconite*. It may be prepared by heating the metal in the air, or by calcining the hydrate, carbonate, or nitrate. It occurs in isometric forms—perhaps also in orthorhombic—but is generally massive. Its specific gravity

is 6.3, and it fuses without change at a bright-red heat. Cupric oxide is easily reduced by both hydrogen and charcoal, with formation of either water or carbon dioxide, and hence is frequently used in organic analysis. *Cupric hydrate* $Cu(OH)_2$ is thrown down as a pale-blue precipitate on adding sodium hydrate to a cold solution of a cupric salt. It acts strongly basic and forms numerous salts.

**165. Cupric Sulphide and Cuprous Sulphide.**—Cupric sulphide $CuS$ is found native as the mineral *covellite*. It is hexagonal in its crystallization, is of bluish-black color, and has a specific gravity of 4.6. It is the black precipitate obtained when copper salts are precipitated by hydrogen sulphide. Cuprous sulphide $Cu_2S$ also occurs native, forming the mineral *chalcocite*. It is the *white metal* obtained in the metallurgy of copper; it may be prepared by exposing finely divided copper or copper foil to sulphur vapor. It crystallizes in orthorhombic prisms, is blackish gray in color, and is easily fusible.

Copper also forms two series of haloid salts, the cuprous $Cu_2F_2$, $Cu_2Cl_2$, and the cupric $CuF_2$, $CuCl_2$, etc. The cuprous halogen salts are insoluble in water, but, like the other cuprous compounds, they are very unstable and readily pass to soluble cupric compounds. Cuprous iodide, however, appears to be more stable than the others, and is precipitated, together with free iodine, when potassium iodide is added to a cupric solution.

**166. Cuprous Chloride.**—Cuprous chloride $Cu_2Cl_2$ is formed together with cupric chloride $CuCl_2$, by burning copper in chlorine, or by the action of reducing agents, such as stannous chloride $SnCl_2$, zinc dust, or metallic copper, on the cupric chloride. If, therefore, cupric oxide is dissolved in concentrated hydrochloric acid, the solution when boiled with excess of copper contains cuprous chloride, which is deposited as a white powder when it is poured into a large quantity of water. This, on exposure to air, turns green, owing to the partial oxidation of the cuprous salt. The solution of cuprous chloride in ammonia or hydrochloric acid

absorbs carbon monoxide and is used for determining the amount of this gas in certain gaseous mixtures. When the ammoniacal solution is acted on by acetylene $C_2H_2$, a basic cuprous acetylide is formed, from which pure acetylene may be liberated by treatment with acid.

**167. Cupric Chloride.**—Cupric chloride $CuCl_2$ is formed by dissolving cupric oxide or carbonate in hydrochloric acid. It crystallizes from aqueous solution in bright-green needles having the composition $CuCl_2, 2H_2O$. These crystals dissolve readily in water or alcohol. When heated, they lose water and yield the anhydrous chloride in the form of a reddish or yellowish brown powder. When dissolved in water, cupric chloride yields a green solution, which changes to blue when diluted. With potassium or ammonium chloride it forms beautiful crystalline double salts.

**168. Cupric Sulphate.**—Cupric sulphate $CuSO_4, 5H_2O$, commonly called *blue vitriol*, is a product of many industrial operations, such as roasting sulphurous copper ores, etc. Cupric sulphate produced by roasting copper ore contains more or less ferrous sulphate. The two salts crystallize together in oblique rhombic prisms, containing 7 molecules of water of crystallization. The mixture is known commercially as *Salzburg vitriol.*

Instead of copper pyrites, artificial cupric sulphide may be oxidized. Old copper plates are moistened and sprinkled with flowers of sulphur; they are then heated in a furnace, and the sulphide of copper first formed is converted into sulphate by the oxygen of the air drawn into the furnace. The still hot plates are plunged into water, which dissolves the layer of cupric sulphate, and the same operation is repeated until all of the metal is transformed into sulphate. The simplest process consists in boiling copper turnings and clippings with sulphuric acid, sulphur dioxide being disengaged and cupric sulphate formed. In the arts, the operation is conducted in lead-lined wooden tanks heated with steam.

Cupric sulphate crystallizes in large, blue, prismatic crystals, which contain 5 molecules of water. When exposed to

dry air, they effloresce superficially; heated to 100°, they lose 4 molecules of water, disengaging the fifth only at 243°. The anhydrous salt is white. At a high heat, cupric sulphate is decomposed into cupric oxide, sulphurous oxide, and oxygen.

Cupric sulphate dissolves in 4 parts of cold and 2 parts of boiling water, and the concentrated solution has a pure blue color. It is insoluble in alcohol.

When an excess of ammonia is added to a solution of cupric sulphate, a beautiful, dark-blue liquid is obtained. It contains ammoniacal cupric sulphate $CuSO_4, 4NH_3, H_2O$, which separates in dark-blue crystals when alcohol is added to the aqueous solution.

There are several basic sulphates of copper representing compounds of cupric sulphate and cupric hydrate. One of them is obtained as a green powder when a solution of cupric sulphate is digested with cupric hydrate. The bluish precipitates obtained by incompletely precipitating solutions of cupric sulphate with potassium hydrate, are basic sulphates.

Cupric sulphate is employed as a caustic applicable to diseases of the eye. In the arts, it is used in the preparation of *blue ashes*, a mixture of calcium sulphate and cupric hydrate, made by decomposing cupric sulphate with milk of lime. It is much used in dyeing, particularly in dyeing black on wool and cotton. It is also employed for preserving wood. Large quantities of sulphate of copper are employed for electrotyping, and for electric batteries.

**169. Carbonates of Copper.**—When cold solutions of sodium carbonate and cupric sulphate are mixed, a bluish-green precipitate is obtained, and at the same time carbonic acid is disengaged. The precipitate becomes green when washed with warm water. It is known as *mineral green*, and can be regarded as a combination of 1 molecule of cupric carbonate with 1 molecule of cupric hydrate. It contains $CuCO_3, Cu(OH)_2$.

A similar compound exists in nature, constituting *malachite*. This mineral occurs in green masses. When cut and polished, it presents veins of various tints, and is fashioned into ornamental objects.

*Azurite*, or *mountain blue*, which crystallizes in beautiful, blue, oblique rhombic prisms, can be regarded as a compound of 2 molecules of cupric carbonate with 1 molecule of the hydrate $2CuCO_3, Cu(OH)_2$.

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## SILVER.

*Symbol Ag. Atomic weight 107.66. Valence I.*

**170. History and Occurrence.**—Silver has been known in the metallic form from the earliest historic times. In it we meet the first metal so far considered that is not capable of undergoing oxidation in the air.

As might be expected from its want of direct attraction for oxygen, silver is found frequently in the metallic, or native, state, crystallized in cubes or octahedrons, which are aggregated together, as in the silver mines of Potosi, into arborescent, or dendritic, forms; it is generally contaminated with copper and gold, and sometimes with mercury. Silver is more frequently met with, however, in combination with sulphur, forming the sulphide of silver $Ag_2S$, which is generally associated with large quantities of the sulphides of lead, antimony, and iron. The United States, Mexico, Australia, and Germany are the principal silver-producing countries, but this metal is widely distributed, and the quantity furnished by South American and other European countries is by no means insignificant. Silver chloride is found in considerable quantity in the spongy deposits of silica around the Great Salt Lake, Utah.

**171. Preparation.**—The process employed for the extraction of silver varies, naturally, with the quality of the ore. At Freiberg, Germany, the ore—an impure sulphide—is roasted with 10 per cent. of salt; the resulting mass is ground to a fine powder, and agitated in revolving barrels containing water and scrap iron, by which the silver chloride is reduced to the metallic state. Mercury is then added to dissolve the silver, and by distilling the amalgam thus obtained the silver is left pure. In this country most of the

silver is obtained in the lead-smelting process, as described in Arts. **132** and **133,** or in connection with gold, by amalgamation, or one of the lixiviation processes.

**172. Properties.**—Pure silver is a remarkably white, lustrous metal of specific gravity 10.5, and is capable of taking a high polish. It is harder than gold, but may be hammered into leaves only one four-thousandth of a millimeter thick, and drawn into wire so fine that 2,000 meters would only weigh 1 gram. It has a high tenacity, the weight of 85 kilograms being required to break a wire of silver 2 millimeters in diameter. It is the best conductor of heat and electricity known. It melts at 954° and may be distilled at the highest temperature of the oxyhydrogen blowpipe. When melted it is capable of absorbing twenty-two times its own volume of oxygen, which, however, is again evolved when it solidifies. It is unaltered in the air at any temperature, though it is readily acted on by chlorine, by sulphur, and by phosphorus. Nitric acid dissolves it easily, hydrochloric and sulphuric acids, however, only difficultly. The alkalies have no action on silver; for this reason silver vessels are used in the laboratory for fusing potassium hydrate and concentrating its solutions. By the action of certain reducing agents on silver salts, the metal is obtained in a finely divided condition, in which form it shows brilliant golden, ruby, blue, and other colored tints.

**173. Uses.**—Owing to its softness, silver is rarely used in the pure state. It is generally alloyed with copper, which, while it greatly increases its hardness, scarcely alters its color. The silver-coin alloy of the United States and France contains 10 per cent. of copper, that of England 7.5 per cent., and that of Germany 12.5 per cent. The silver used in silver plate usually contains from 70 to 95 per cent. of pure silver.

The operation of *silvering*, as its name indicates, consists in covering the common metals or glass with a coating of silver of greater or less thickness.

The metals are silvered by either amalgamation or galvanic

deposition. In the latter and much more preferable operation, a solution of the double cyanide of silver and potassium is generally used.

Mirrors and glass articles in general are silvered by the reduction of a silver salt by aldehyde, glucose, or tartaric acid. The following recipe is given by Liebig: A solution of 10 grams of silver nitrate is supersaturated with ammonia and sodium hydrate is added. The volume of the liquid should be 1,450 cubic centimeters. Another solution is prepared by dissolving 1 part of milk sugar in 10 parts of water. The latter solution is mixed with its own volume of the first solution, and the glass to be silvered is washed with alcohol and immersed in the liquid. The reduction of the silver salt begins immediately, and does not require the aid of heat.

The experiment may be easily made in a small glass flask, the interior of which will be uniformly silvered.

*Electroplating* consists of covering the surface of baser metals with a coating of silver, by connecting them with the negative (or zinc) pole of the galvanic battery, and immersing them in a solution made by dissolving silver cyanide in potassium cyanide (a solution of potassium cyanide in 10 parts of water, with 3.5 grams of silver chloride dissolved in each pint of the liquid, will answer the purpose nicely), the positive (copper or platinum) pole being connected with a silver plate, also immersed in the solution. The electric current gradually decomposes the silver cyanide, and this metal is deposited upon the object connected with the negative electrode, while the cyanogen liberated at the silver plate attacks the silver, so that the solution is always maintained at the same strength, the quantity of silver dissolved at this electrode being precisely equal to that deposited at the opposite one.

## COMPOUNDS OF SILVER.

**174. Silver Oxide.**—Silver oxide $Ag_2O$ is usually prepared by adding a strong, hot solution of silver nitrate to one of potassium hydroxide. It is also the product of the combustion of silver at high temperatures. It is a

dark-brown powder with a specific gravity of 7.2. It is readily decomposed by heat, and partially by light, into metallic silver and oxygen. It is only slightly soluble in water; ammonia dissolves it readily, the solution depositing a violently explosive crystalline compound, probably the nitride $Ag_3N$.

**175. Silver Sulphide.**—To the oxide of silver corresponds the sulphide $Ag_2S$, which occurs native as *argentite* or *argentine*, crystallized in regular octahedrons. It is soft, and can be scratched with the finger nail. It is prepared either by heating together silver and sulphur or by precipitating silver salts with hydrogen sulphide.

**176. Silver Fluoride.**—Silver fluoride $AgF$ is formed when the oxide or carbonate is dissolved in hydrofluoric acid. It crystallizes from water as $AgF, H_2O$ or $AgF, 2H_2O$. It is soluble in little more than half its weight of water, the solution having a strongly alkaline reaction. The salt readily takes up ammonia, and is reduced to the metallic state by it when heated.

**177. Silver Chloride.**—Silver chloride $AgCl$ occurs native as the mineral *cerargyrite*. It may be obtained by the direct union of silver and chlorine, or by precipitating a solution of silver nitrate by a chloride. A white, curdy mass, soluble in ammonium hydrate, but insoluble in nitric acid, is thrown down, which on drying becomes a white powder. When heated it fuses, and on cooling solidifies to a crystalline, translucent, sectile mass resembling horn, whence the name *horn silver*, sometimes applied to it. It has a specific gravity of 5.4, crystallizes in isometric forms, and turns black on exposure to light. For the latter reason it is used in photography.

If recently precipitated and moist silver chloride is placed upon a sheet of zinc, in a short time a dark color will appear on the borders of the chloride, and the whole of that body will soon be converted into a dark-gray powder of finely divided silver, zinc chloride being at the same time formed.

This reaction takes place much more rapidly if the silver chloride is moistened with hydrochloric acid. In this case the reduction is effected by nascent hydrogen produced by the action of the hydrochloric acid on the zinc.

**178. Silver bromide** $AgBr$ and **silver iodide** $AgI$ are both found in nature in Mexico and Chile.

Silver bromide may be obtained on adding hydrobromic acid, or a bromide of an alkali metal, to a solution of silver nitrate, as a yellowish-white, curdy precipitate, which is insoluble in nitric acid and is less soluble in dilute ammonia than is the chloride. In other respects it is similar to the chloride. When suspended in water, it is easily decomposed by chlorine; hydrochloric-acid gas also decomposes it at 700°, with the evolution of hydrobromic acid. The precipitated bromide when exposed to light changes its color and assumes a grayish tint.

Silver iodide is a yellow precipitate, produced by adding silver nitrate to potassium iodide. It is insoluble, or nearly so, in ammonia, and in this respect forms an exception to silver salts in general. It blackens on exposure to light.

**179. Silver Nitrate.**—Silver nitrate $AgNO_3$, or *lunar caustic* [silver being distinguished as *luna* (the moon) by the alchemists], is procured by dissolving silver in nitric acid, with the aid of a gentle heat, evaporating the solution to dryness, and heating the residue until it fuses, in order to expel the excess of acid. It fuses at 218°. For use in surgery, the fused nitrate is poured into cylindrical molds, so as to cast it into thin sticks; but for chemical purposes it is dissolved in water and crystallized, when it forms colorless, square tables of specific gravity 4.3, easily soluble in water and alcohol. The action of nitrate of silver as a caustic depends on the facility with which it parts with oxygen, the silver being reduced to the metallic state, and the oxygen combining with the elements of the organic matter. This effect is very much promoted by exposure to sunlight, or diffused daylight. Pure silver nitrate is not changed by exposure to light, but if organic matter is present, a black

deposit, containing finely divided silver, is produced. Thus the solution of silver nitrate stains the fingers black when exposed to light, but the stain may be removed by potassium cyanide, or, more safely, by tincture of iodine. If a solution of silver nitrate is dropped upon paper and exposed to light, black stains will be produced and the paper corroded. Silver nitrate is frequently a constituent of the so called marking inks, since the deposit of metallic silver formed on exposure to light is not removable by washing.

In order to prepare silver nitrate from standard silver (containing copper), the metal is dissolved in moderately strong nitric acid, and the solution evaporated to dryness in a porcelain dish, when a blue residue containing the nitrates of silver and copper is obtained. This dish is now moderately heated until the residue has fused, and become uniformly black, the blue copper nitrate being decomposed and leaving black copper oxide, at a temperature that is insufficient to decompose the silver nitrate. To ascertain when all the copper nitrate is decomposed, a small sample is removed on the end of a glass rod, dissolved in water, filtered and tested with ammonia, which will produce a blue color if any copper nitrate is left. The residue is treated with hot water, the solution filtered from the copper oxide and evaporated to crystallization.

Silver nitrate forms crystalline double salts with 1 molecule of potassium or ammonium nitrate. It absorbs ammonia with evolution of heat, and *silver ammonio-nitrate* $AgNO_3,2NH_3$ may be crystallized from a strong solution of silver nitrate saturated with ammonia.

**Silver nitrite** $AgNO_2$ is obtained as a white precipitate by treating a strong solution of silver nitrate with potassium nitrite. It is soluble in water and crystallizes in prismatic crystals. By long boiling with water it is decomposed:

$$2AgNO_2 = AgNO_3 + Ag + NO$$

**180. Silver Carbonate.**—Silver carbonate $Ag_2CO_3$ is obtained in transparent yellow crystals when moist silver oxide is acted on by carbonic acid. It dissolves in solution

of carbonic acid like $CaCO_3$, and is deposited in crystals when exposed to the air. It is feebly alkaline to moist test paper. It bears heating to a large extent, and fuses just before decomposition.

**181. Silver sulphate** $Ag_2SO_4$ is obtained by roasting $Ag_2S$ in air. It forms a white crystalline precipitate when a strong solution of silver nitrate is stirred with dilute sulphuric acid. It is soluble in water and fuses at 654°.

**Silver sulphite** $Ag_2SO_4$ forms a white precipitate when sulphurous acid is added to silver nitrate. Boiling with water reduces it to metallic silver:

$$Ag_2SO_3 + H_2O = Ag_2 + H_2SO_4$$

**Silver orthophosphate** $Ag_3PO_4$ is formed as a yellow precipitate when sodium phosphate is added to silver nitrate:

$$Na_2HPO_4 + 3AgNO_3 = 2NaNO_3 + HNO_3 + Ag_3PO_4$$

It is soluble in nitric acid and in ammonia.

**Silver arsenite** $Ag_3AsO_3$ is obtained as a yellow precipitate by adding a silver-nitrate solution to a solution of sodium arsenite. If the precipitate at first formed is almost white, a few drops of ammonia should be added, but the precipitate dissolves in a larger quantity of ammonia, and in nitric acid.

**Silver arsenate** $Ag_3AsO_4$ is obtained as a reddish-brown precipitate when silver nitrate is added to a sodium-arsenate solution. It is soluble in nitric acid, and in ammonia.

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## MERCURY.

*Symbol Hg. Atomic weight 199.8. Valence I and II. Density 99.9. Molecular weight 199.8. One liter of mercury vapor weighs 8.96 grams (99.9 criths).*

**182. History and Occurrence.**—Mercury has been known from the earliest times; its Latin name *argentum vivum*, of which the English name *quicksilver* is a literal translation, refers to its fluidity as well as to its color. The

name mercury, from the planet of that name, was given by the alchemist to all volatile substances, but only this one has retained it. The symbol of mercury *Hg* is derived from the Latin name ***hydrargyrum***. Mercury occurs native only sparingly, the chief ore being the sulphide, called ***cinnabar***, which is found principally in Idria, in Austria; Almaden, in Spain; and New Almaden, in California.

**183. Preparation.**—The process of extracting the mercury from its ore is a rather simple and easy one. It usually consists in roasting the ore in a reverberatory furnace, or even a small blast furnace, with access of air, by which the sulphur is oxidized to sulphur dioxide, and the mercury set free and volatilized, according to the equation:

$$HgS + O_2 = Hg + SO_2$$

Sometimes lime or oxide of iron is mixed with the ore, and the sulphur retained in this way is sulphide of lime or of iron, depending on which has been used. The condensation of the vapors of mercury is, however, a matter of some difficulty, and the methods employed vary considerably in different localities.

At Idria, the vapors are passed through chambers and a series of twin tubes of cast iron cooled externally by water. They are so arranged that the condensed metal collects and runs down into the receptacle at the base of each tube. In Almaden, twelve parallel series of conical clay receivers, called *aludels*, luted together, are interposed between the furnace and its flue; each of these is about 20 inches long, and a series extends about 20 yards. The lines of aludels are of sufficient length to allow the vapors and gases to cool down nearly to the temperature of the air, and so arranged as to allow the condensed mercury to gravitate towards a common channel where it collects.

**184. Properties.**—Mercury is a brilliant, silver-white metal. It has a specific gravity of 13.59 at 0° and is the only metal that is liquid at the ordinary temperatures. Cooled to

$-40°$, it solidifies to a malleable, tin-white mass, easily sectile, and crystallizing in regular octahedrons. Even at ordinary temperatures mercury has a small vapor tension, and gives off minute quantities of its vapor into the atmosphere in contact with it. It boils at 350°, yielding a colorless vapor of specific gravity 6.976. When heated almost to its boiling point in air, it becomes coated with the red oxide $HgO$. It is unaltered in air; neither hydrochloric nor dilute sulphuric acid attacks it, but boiling, strong sulphuric acid, or even dilute nitric acid, dissolves it readily. Chlorine and sulphur unite directly with it.

Mercury is used in the arts for filling thermometers and barometers, and very extensively for extracting gold and silver from their ores. With most of the metals it forms alloys, known as *amalgams*, and in some cases these amalgams possess a definite composition and crystalline form, e. g., $Hg_6Na$ is brittle and crystallizes in regular forms. Sodium amalgam is a convenient reducing agent, for when brought into contact with water or solutions in water, hydrogen is evolved. Tin amalgam is used for producing the silver coating on glass for mirrors.

Mercury forms two series of compounds, the mercurous, in which this metal is monovalent, and the mercuric, in which it is divalent. It will be seen that the two series differ very considerably in properties.

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## COMPOUNDS OF MERCURY.

**185. Mercurous Oxide.**—Mercurous oxide $Hg_2O$ is a dark-brown or black powder obtained by digesting mercurous chloride $Hg_2Cl_2$ (calomel) with potassium hydrate or by adding an alkaline hydrate to a mercurous solution. It is very unstable, and is even decomposed by the action of light or heat into mercuric oxide and metallic mercury.

**186. Mercuric Oxide.**—Mercuric oxide $HgO$ may be prepared by either a dry or wet method. The dry consists in decomposing mercuric nitrate by heat; the salt is gradually

heated in a flask on a sand bath until vapors cease to be disengaged. The oxide thus prepared is an orange-red, granular, and crystalline powder. In the wet way, mercuric oxide is prepared by decomposing a solution of mercuric chloride by potassium hydrate, a yellow precipitate of anhydrous mercuric oxide being thus obtained.

When mercuric oxide is heated, it assumes a dark-red color and decomposes, if the temperature is above 400°, into oxygen and mercury. Mercuric oxide is soluble in acids, yielding mercuric salts.

**187. Mercuric Sulphide.**—Mercuric sulphide $HgS$ occurs in nature as the mineral cinnabar, both massive and in rhombohedral crystals. It is obtained artificially by direct synthesis. The combination takes place when the elements are triturated in the cold, in the proportion of 100 parts of mercury and 18 parts of sulphur. A black mass is thus obtained, which is sublimed in iron vessels.

The pigment *vermilion* is a finely divided mercuric sulphide, having a beautiful rich scarlet color. It is prepared by triturating for several hours, in a mortar, 300 parts of mercury and 114 parts of flowers of sulphur, and adding to the black sulphide thus obtained 75 parts of potassium hydrate and 400 parts of water. The mixture is maintained at a temperature of about 45°, being continually triturated with a pestle. As soon as the powder has acquired a fine scarlet color, it is rapidly washed with hot water and dried. It is employed in painting, coloring sealing wax, and for various other purposes.

**188. Mercuric Nitride.**—Mercuric nitride $Hg_3N_2$ is obtained by gently heating to about 130° dry yellow mercuric oxide in a current of ammonia gas:

$$3HgO + 2NH_3 = Hg_3N_2 + 3H_2O$$

By the action of dilute ammonia on yellow mercuric oxide, *Millon's base* is formed. This compound has the composition $NHg_2OH, H_2O$, and by gently heating is transformed into the anhydrous $(NHg_2)_2O$. These substances in the dry state

are very unstable and liable to decompose with explosion, yet they are so strongly basic as to resemble the caustic alkalies, expelling ammonia from its compounds, absorbing carbon dioxide very freely, and only undergoing decomposition when fused with potash or soda. $NHg_2OH,H_2O$ forms a well defined series of salts in which the $OH$ group is replaced by the acid radical.

**189. Mercurous Chloride.**—Mercurous chloride $Hg_2Cl_2$, ordinarily called *calomel*, is precipitated whenever a chloride is added to a solution of a mercurous salt. It occurs in nature in tetragonal prisms. Commercially, it is prepared by subliming a mixture of mercuric sulphate, mercury, and salt:

$$HgSO_4 + Hg + 2NaCl = Na_2SO_4 + Hg_2Cl_2$$

The heavy white powder that condenses is washed with water to remove any mercuric chloride. It is not soluble in water, though chlorine water and nitric acid dissolve it by converting it into mercuric chloride. It volatilizes below a red heat, yielding 4 volumes of vapor, being decomposed into mercuric chloride and free mercury. Calomel is gradually decomposed by light, and is blackened by ammonium hydroxide.

**190. Mercuric Chloride.**—Mercuric chloride $HgCl_2$, also known as *bichloride of mercury* or *corrosive sublimate*, is manufactured by heating 2 parts by weight of mercury with 3 parts of strong sulphuric acid, and evaporating to dryness, to obtain mercuric sulphate:

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$$

which is mixed with 1½ parts of common salt and heated in a large glass vessel:

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$$

when sodium sulphate is left, and the corrosive sublimate is converted into vapor, condensing on the cooler part of the vessel in lustrous, colorless masses, which have a crystalline structure and a specific gravity of 5.4. Mercuric chloride

fuses at 288° to a perfectly colorless liquid, which boils at 303°, emitting an extremely acid vapor, which destroys the sense of smell for some time. This vapor condenses in fine needles, or sometimes in octahedrons. Corrosive sublimate dissolves in twice its weight of boiling water, but requires 16 parts of cold water, so that the hot solution readily deposits crystals of the salt on cooling. It is somewhat remarkable that corrosive sublimate is much more easily dissolved by alcohol and ether than by water; boiling alcohol dissolves about an equal weight of the mercuric chloride, and cold ether takes up about one-third of its own weight. By shaking the aqueous solution with ether, the greater part of the corrosive sublimate will be removed, and will remain dissolved in the ether, which rises to the surface. An aqueous solution of ammonium chloride will take up corrosive sublimate more easily than will pure water, a soluble double chloride (*sal alembroth*) being formed, which may be obtained in tabular crystals of the composition $HgCl_2,2NH_4Cl,H_2O$. A solution of corrosive sublimate in water containing sal ammoniac is a very efficacious bug poison.

Sulphuric acid does not decompose mercuric chloride, though it attacks mercurous chloride. Hydrochloric acid combines with it, forming crystalline compounds, $HCl,HgCl_2$ and $HCl,2HgCl_2$, which lose $HCl$ when exposed to air.

Mercuric chloride is very poisonous, as little as 200 milligrams having been known to cause death to a child. The white of egg is commonly administered as an antidote, owing to the fact that it forms an insoluble compound with this poison and thus renders it inert to the stomach. The compound of albumin with corrosive sublimate is also much less liable to putrefaction than albumin itself, and hence corrosive sublimate is sometimes employed for preserving anatomical specimens and for preventing the decay of wood (by combining with the vegetable albumin of the sap). Mercuric chloride unites with many other chlorides to form soluble double salts, and with mercuric oxide, forming several oxychlorides, which, however, have no useful application in science or in the arts.

Mercuric chloride is said to occur naturally in one of the Molucca Islands.

*White precipitate*, employed for destroying vermin, is deposited when ammonia is added to a solution of corrosive sublimate, according to the equation:

$$HgCl_2 + 2NH_4OH = NH_4Cl + 2H_2O + NH_2Hg''Cl$$

It may be regarded as the chloride of mercury ammonium: that is, ammonium chloride in which 2 atoms of hydrogen are replaced by 1 atom of the divalent mercury, or as amido-mercuric chloride in which one bond of the divalent mercury is attached to the monovalent amido group $NH_2$, while the other is united to an atom of chlorine. The solutions of corrosive sublimate possess powerful antiseptic properties.

**191. Mercurous Iodide.**—Mercurous iodide $Hg_2I_2$ is, as a rule, prepared by direct synthesis, 100 parts of mercury and 63.5 parts of iodine being triturated with a small quantity of alcohol, until the whole is converted into a green powder, which is then washed with boiling alcohol and dried. It may also be obtained by precipitating a mercurous salt with potassium iodide.

Mercurous iodide is a rather unstable compound, being decomposed by light as well as by heat, the latter breaking it up into mercury and mercuric iodide. The same decomposition is effected by potassium iodide and the alkaline chlorides.

**192. Mercuric Iodide.**—Mercuric iodide $HgI_2$ is prepared by pouring a solution of 100 parts of potassium iodide into a solution of 80 parts of corrosive sublimate $HgCl_2$. A scarlet-red precipitate of mercuric iodide is thrown down.

It is absolutely necessary that these compounds are mixed in exactly the proportions given; an excess of potassium iodide would dissolve the mercuric iodide first precipitated.

Mercuric iodide is nearly insoluble in water; it is slightly soluble in boiling alcohol, which deposits it, on cooling, in small, red, octahedral crystals.

On heating, mercuric iodide melts to a dark-yellow liquid which solidifies, when cooled, to a yellow mass. At a higher temperature the liquid boils and its vapor condenses to a dark-yellow liquid, which solidifies to a yellow mass; at the same time, right rhombic prisms of a yellow color sublime. If these are rubbed with a glass rod or other hard substance they instantly become red, first at the point of contact, then throughout the entire mass.

Mercuric iodide forms a combination with potassium iodide that is soluble in water. A solution of this potassium mercuric iodide is not precipitated by potassium hydrate, but the liquid rendered alkaline by the latter compound is a very sensitive test for ammonia (Nessler's test), with which it gives a precipitate or a brown cloud more or less intense, according to the quantity of ammonia present.

**193. Mercuric Cyanide.**—Mercuric cyanide $Hg(CN)_2$ is of importance in that it is the salt that, on being heated, yields cyanogen gas (an organic compound). It may be prepared by boiling mercuric sulphate and potassium ferrocyanide together in aqueous solution. It crystallizes in white needles and is soluble in about 8 parts of cold water.

**194. Sulphates of Mercury.**—There is a *mercurous sulphate* $Hg_2SO_4$ and a *mercuric sulphate* $HgSO_4$, obtained by heating together mercury and sulphuric acid, the particular one formed depending on whether excess of mercury or sulphuric acid, respectively, is used. The mercuric sulphate is the more important salt. It consists of white crystals, which, on heating, undergo decomposition with the formation of mercurous sulphate. In presence of water the salt is apt to become basic. *Turpeth mineral* is a yellow basic sulphate, $2HgO, Hg_2SO_4$, obtained by digesting mercuric sulphate with boiling water.

**195. Nitrates of Mercury.**—*Mercurous nitrate* $HgNO_3$ and *mercuric nitrate* $Hg(NO_3)_2$ are formed from mercury and nitric acid under similar conditions to the sulphates, and, like them, form basic salts in presence of water.

For the weaker acids the affinity of mercury is too feeble to admit the formation of stable salts; the phosphates, carbonates, borates, and silicates have been either not prepared at all, or are obtained as basic compounds of variable composition.

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## PLATINUM.

*Symbol Pt. Atomic weight 194.8. Valence II, IV, and VI.*

**196. History and Occurrence.**—Platinum was taken to Europe from South America, in 1735, by Ulloa, and, in 1741, by Wood. It was first described by Watson, in 1750, and independently by Scheffer, in 1752. It derives its name from the word *platina*, the Spanish diminutive of *plata*, "silver." It is found distributed in flattened grains through alluvial deposits similar to those in which gold is found; in fact, these grains are generally accompanied by grains of gold, and of a group of very rare elements only found in platinum ores; viz., *palladium*, *iridium*, *osmium*, *rhodium*, and *ruthenium*. Russia furnishes the largest supply of platinum from the Ural Mountains, though smaller quantities are obtained from Brazil, Peru, Borneo, Australia, and California.

**197. Preparation.**—The process for obtaining the platinum in a marketable form is rather a chemical than a metallurgical operation. Native platinum was formerly purified by the method of Wollaston, which consists in first heating the ore containing the grains of platinum and the associated metals with hydrochloric acid, in order to dissolve the base metals, and then in retorts with aqua regia, which dissolves palladium, rhodium, platinum, and a little iridium as chlorides. The osmium in the ore partly distils over as osmic acid and partly remains undissolved as an alloy with the iridium (*osmiridium*), together with ruthenium, chrome iron ore, and titanic iron. The solution containing the platinum as $PtCl_4$ is neutralized with $Na_2CO_3$, and the palladium is precipitated as cyanide $Pd(CN)_2$ by the addition of mercuric cyanide.

The platinum is now precipitated by the addition of ammonium chloride, with which platinic chloride combines to form a yellow salt, ammonium platinochloride $(NH_4)_2PtCl_6$ or $PtCl_4, 2NH_4Cl$.* This precipitate is collected and heated to redness, when all its constituents, except the platinum, are expelled in the form of gas, that metal being left in the peculiar porous condition in which it is known as *spongy platinum*. This is condensed into a cake by powerful pressure, and is then welded at a white heat into a homogeneous mass.

Lately, however, Deville's method has almost entirely superseded that of Wollaston. In this the crude platinum is melted with an equal weight of lead sulphide and half its weight of metallic lead; in this way the platinum is dissolved, leaving a mixture of iridium, rhodium, osmium and ruthenium, known as *iridosmine*. The platinum-lead alloy is then melted and exposed to a current of air (cupelled), by which the lead is oxidized, the oxide volatilizing and the platinum being left as a porous mass. This is then placed in a furnace made of lime (Fig. 9), and by means of two powerful oxyhydrogen jets, it is melted and cast into ingots. Masses weighing 100 kilograms have been produced by this process at one fusion.

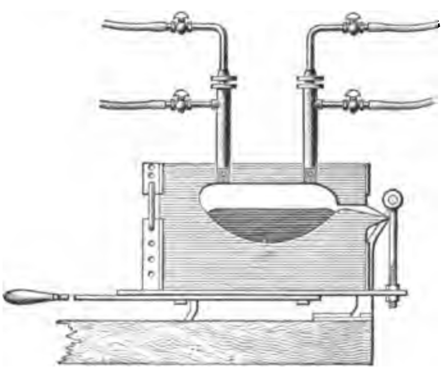

FIG. 9.

**198. Properties.**—Platinum is a brilliant white metal with a tinge of blue. It is remarkable for (1) its high

* When rhodium is present, the liquid from which this precipitate has been deposited will have a rose color. The precipitate is then mixed with bisulphate of ammonium and heated to redness in a platinum dish. The rhodium is then converted into a double sulphate of rhodium and potassium, which may be removed from the spongy platinum by boiling with water.

specific gravity of 21.5; (2) its very high fusing point, 1,775°; (3) its slight expansion when heated, which allows it to be sealed into glass without cracking by unequal contraction on cooling; (4) its being unchanged by air at all temperatures; (5) its resistance to the action of strong acids; (6) its power of inducing the combination of oxygen with other bodies; (7) its being found in nature only in the metallic state.

Its resistance to the action of high temperatures and most chemical agents renders platinum of the greatest service in chemical operations. In the form of basins, small crucibles, foil, and wire, it is indispensable to the analytical chemist. Unfortunately, it is softer than silver, and therefore ill adapted for wear, and is so heavy that even small vessels must be made very thin in order not to be too heavy for a delicate balance. Commercial platinum generally contains a little iridium, which hardens it and increases its elasticity. Its malleability and ductility are very considerable, so that it is easily rolled into thin foil and drawn into fine wires; in ductility it is surpassed only by gold and silver, and it has been drawn by an ingenious contrivance of Wollaston's into wire of only $\frac{1}{30000}$ of an inch in diameter, a mile of which, notwithstanding the high specific gravity of the metal, would only weigh 1 grain. This remarkable extension of the metal was effected by casting a cylinder of silver around a very thin platinum wire obtained by the ordinary process of wire drawing; when the cylinder of silver, with the platinum wire in its center, was itself drawn out into an extremely thin wire, of course the platinum core would have become inconceivably thin, and when the silver casing was dissolved off by nitric acid, this minute filament of platinum was left.

Platinum possesses the remarkable power of inducing chemical combination between oxygen and other gases. Even the compact metal possesses this property, as may be seen by heating a piece of platinum foil to redness in the flame of a gauze gas burner, rapidly extinguishing the gas, and turning it on again, when the cold stream of gas will still maintain the metal at a red heat, in consequence of the

combination with atmospheric oxygen at the surface of the platinum.

A similar experiment may be made by suspending a coil of platinum wire in the flame of a spirit lamp and suddenly extinguishing the flame, when the metal is intensely heated, by placing the mouth of a test tube over it; the wire will continue to glow by inducing the combination of the spirit vapor with oxygen on its surface. By substituting a little ball of spongy platinum for the coil of platinum wire and mixing some fragrant essential oil with the spirit, a very effective perfuming lamp has been contrived. Upon the same principle an instantaneous light apparatus has been constructed, in which a jet of hydrogen gas is kindled by falling upon a fragment of cold, spongy platinum, which at once ignites it by inducing its combination with the oxygen condensed within the pores of the metal (Döbereiner's lamp). Spongy platinum is obtained in a very active form by heating the ammonio-chloride of platinum very gently in a stream of coal gas or hydrogen as long as any fumes of hydrochloric acid are evolved.

If platinum is precipitated in the metallic state from a solution, it is obtained in the form of a powder called *platinum black*, which possesses this power of promoting combination with oxygen in the highest perfection. This form of platinum may be obtained by boiling a solution of platinic chloride with Rochelle salt (potassium-sodium tartrate), or by dropping it into a boiling mixture of 3 volumes of glycerine and 2 volumes of $KOH$ of specific gravity 1.08, when the platinum black is precipitated, and must be filtered off, washed, and dried at a gentle heat.

Platinum in this form is capable of absorbing 800 times its volume of oxygen, which, however, does not enter into combination with it, but is simply condensed into its pores, and is available for combination with other bodies. A jet of hydrogen allowed to pass on to a grain or two of this powder is kindled at once, and, if a few particles of it are thrown into a mixture of hydrogen and oxygen, explosion immediately follows. A drop of alcohol is also inflamed when allowed to

fall on a little of the powder. Platinum black loses its activity after having been heated to redness. It has been stated that platinum black is really an oxide, and that the combustion of hydrogen and oxygen in presence of platinum is to be explained by the formation at first of an unstable hydride of platinum, with the development of heat, which is oxidized with a still further development of heat. By a continued repetition of the changes, the platinum is raised to the temperature necessary for ignition.

Although platinum resists the action of hydrochloric and nitric acids unless they are mixed, and is unaffected, at the ordinary temperature, by other chemical agents, it is easily attacked at high temperatures by phosphorus, arsenic, carbon, boron, silicon, and by a large number of metals; the caustic alkalies and alkaline earths also corrode it when heated, so that some discretion is necessary in the use of vessels made of this rather costly metal.* When platinum is alloyed with 10 parts of silver, both metals may be dissolved by nitric acid.

If platinum is dissolved in 4 or 5 parts of melted tin, and the alloy boiled with hydrochloric acid mixed with an equal bulk of water, glistening scales are left, resembling graphite and soiling the fingers. This body contains platinum, tin, chlorine, hydrogen, and oxygen. By treatment with warm dilute ammonia, it becomes brownish, and, when dried in a vacuum over sulphuric acid, has the composition $Pt_2Sn_3O_4H_2$. When this is heated in dry oxygen, it becomes $Pt_2Sn_3O_4$. Heated in hydrogen, it leaves a grayish, almost infusible, powder containing $Pt_2Sn_3$.

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## COMPOUNDS OF PLATINUM.

**199. Oxides of Platinum.**—Only one oxide of platinum is known in the free state, the other having been obtained only in combination with water. *Platinous oxide* $PtO$

* Platinum leaf when heated with $HCl$ at 150° in a sealed tube is dissolved, but the chloride is subsequently reduced by the hydrogen evolved, and the metal reappears as crystals on the side of the tube. The same has been observed of gold and silver leaf.

is precipitated as a black hydrate by decomposing platinous chloride with potash, and neutralizing the solution with dilute sulphuric acid. It is a feeble base and decomposes when heated, leaving metallic platinum. *Platinic oxide* $PtO_2$ is also a weak base, but is characteristically an acid oxide.

*Platinic hydroxide* $Pt(OH)_4$ is obtained by boiling platinic chloride with potash, and treating the precipitate with acetic acid; this leaves a nearly white powder $Pt(OH)_4,2H_2O$. At 100° this becomes brown, $Pt(OH)_4$. Acid dissolves it, forming platinic salts. Alkalies dissolve it, forming platinates. Heat reduces the oxides and hydroxides to metallic platinum.

*Sodium platinate* $Na_2O,3PtO_2,6Aq$ may be crystallized from a solution of the hydroxide in soda. *Calcium platinate* is convenient for the separation of platinum from iridium, which is generally contained in the commercial metal; for this purpose, the platinum is dissolved in nitrohydrochloric acid, the solution evaporated till it solidifies on cooling, the mixed chlorides of platinum and iridium dissolved in water, and decomposed with an excess of lime *without exposure to light;* the platinum then passes into solution as calcium platinate, and the platinic acid may be separated as calcium salt from the filtered solution by exposure to light. If platinic hydroxide is dissolved in diluted sulphuric acid and the solution mixed with excess of ammonia, a black precipitate of *fulminating platinum* is obtained, which detonates violently at about 204°. This compound is said to have a composition corresponding with the formula $N_2H_2Pt^{iv},4H_2O$ ; or, in other words, it is a combination of water with a double molecule of ammonia $N_2H_6$ in which 4 atoms of $H$ have been replaced by 1 atom of quadrivalent platinum.

**200. Chlorides of Platinum.**—*Platinic chloride* $PtCl_4$, also known as *perchloride of platinum*, is the most important salt of this metal. It may be prepared by dissolving scraps of platinum foil in a mixture of 4 parts by volume of hydrochloric acid with 1 part nitric acid, evaporating the liquid at a gentle heat to the consistence of syrup, redissolving in

hydrochloric acid, and again evaporating to expel excess of nitric acid. The syrupy liquid solidifies, on cooling, to a red-brown mass, which is very deliquescent, and dissolves easily in water or alcohol to a red-brown solution. If the concentrated solution is allowed to cool before all the free hydrochloric acid has been expelled, long, brown, prismatic crystals, of a combination of platinic chloride with hydrochloric acid $PtCl_4,2HCl,6Aq$, are obtained. If these are heated in dry $HCl$, the anhydrous $PtCl_4$ is obtained in a non-deliquescent condition; it decomposes $Na_2CO_3$, evolving $CO_2$. Platinic chloride is remarkable for its disposition to form sparingly soluble double chlorides with the chlorides of the alkali metals and the hydrochlorides of organic bases—a property of great value to the chemist in effecting the detection and separation of these bodies. These double chlorides are generally regarded as *platinochlorides* or *chloroplatinates*, derived from hydrogen *platinochloride* or *chloroplatinic acid* $H_2PtCl_6$.

A good example of this has been afforded in the separation of potassium, rubidium, and cæsium. The chlorides of these three metals, having been separated from the various other salts contained in the mineral water in which they occur, are precipitated with platinic chloride, which forms combinations with all three chlorides. The platinochloride of potassium is more easily dissolved by boiling water than are those of rubidium and cæsium, and is removed by boiling the mixed precipitate with small portions of water as long as the latter acquires a yellow color. The remaining platinochlorides of rubidium and cæsium are then heated in a current of hydrogen, which reduces the platinum to the metallic state, and the chlorides may then be extracted by water, in which they are very soluble.

*Potassium platinochloride* $K_2PtCl_6$ or $2KCl,PtCl_4$ forms minute yellow octahedral crystals; the crystals of rubidium and cæsium have a similar composition and a crystalline form. *Sodium platinochloride* differs in being very soluble in water and alcohol; it may be crystallized in long red prisms, having the composition $Na_2PtCl_6,6Aq$ or $2NaCl,PtCl_4,6Aq$. *Ammonium platinochloride* $2NH_4Cl,PtCl_4$ or $(NH_4)_2PtCl_6$ has

been already noticed in Art. **197** as the form in which platinum is precipitated in order to separate it from other metals. It crystallizes like the potassium salt, in yellow octahedrons, which are very sparingly soluble in water and entirely insoluble in alcohol. It is the form into which nitrogen is finally converted in analysis in order to determine its weight. When heated to redness, this salt leaves a residue of spongy platinum. Silver nitrate, added in excess to platinic chloride containing $HCl$, precipitates all the platinum as $2AgCl,PtCl_2$, a yellow precipitate decomposed by water.

Platinic chloride is sometimes sold under the name of *muriate of platina*, for browning gun barrels, etc.

*Platinous chloride* $PtCl_2$, also known as *protochloride of platinum*, is obtained by heating platinic chloride to above 232°, when the latter is decomposed (with the evolution of chlorine) into platinous chloride, which, in its turn, by a continuously raised heat, is again slowly decomposed into metallic platinum and chlorine. Platinous chloride forms a dingy-green powder, which is insoluble in water, in nitric or sulphuric acid. It dissolves, however, in hot hydrochloric acid, and in a solution of platinic chloride, yielding a solution in the former case of a bright red, and in the latter of a dark brownish red. Platinous chloride is capable of absorbing ethylene $C_2H_4$. At 250° it absorbs $CO$ and forms the crystalline volatile compounds $PtCl_2CO$, $PtCl_2(CO)_2$, and $(PtCl_2)_2(CO)_3$, and the non-volatile compound $PtCl_2,2COCl_2$. Its solution in hydrochloric acid is not precipitated by potassium chloride, but a soluble double chloride, $2KCl,PtCl_2$, may be crystallized from this liquid. If ammonium chloride is added to the hydrochloric solution, a double salt, *ammonium chloroplatinite* $2NH_4Cl,PtCl_2$, may be obtained in yellow crystals by evaporation. If, instead of ammonium chloride, free ammonia is added in excess to the boiling solution of platinous chloride in hydrochloric acid, brilliant green needles (known as *green salt of magnus*) are deposited on cooling, which contain the elements of platinous chloride and ammonia $PtCl_2(NH_3)_2$; but from the behavior of this compound with chemical agents, its true formula would

appear to be $N_2H_6Pt''Cl_2$, in which the place of 2 atoms of hydrogen in 2 molecules of ammonium chloride is occupied by divalent platinum. By heating this salt with an excess of ammonia, the solution, on cooling, deposits yellowish-white crystals of *diplatosamine hydrochloride* $N_4H_{10}Pt'',2HCl,Aq$, the production of which may be represented by the equation:

$$N_2H_6Pt''Cl_2+2NH_3 = N_4H_{10}Pt'',2HCl$$

By decomposing a solution of this salt with silver sulphate the diplatosamine sulphate $N_4H_{10}Pt'',H_2SO_4$ is obtained according to the subjoined equation:

$$N_4H_{10}Pt'',2HCl+Ag_2SO_4 = N_4H_{10}Pt'',H_2SO_4+2AgCl$$

When this solution of diplatosamine sulphate is treated with barium hydroxide, barium sulphate is precipitated, and a powerfully alkaline solution is obtained, which yields crystals of *hydrated diplatosamine* $N_4H_{10}Pt'',2H_2O$, a strong alkali which may be regarded as a compound of water with 4 molecules of ammonia $N_4H_{12}$, in which 2 atoms of hydrogen are replaced by platinum. The hydrated diplatosamine has a strong resemblance to the alkalies, eagerly absorbing carbon dioxide from the air, and expelling ammonia from its salts. When the hydrated diplatosamine is heated to 110° it gives off water and ammonia, and becomes converted into a gray, insoluble substance, which is *hydrated platosamine* $N_2H_4Pt'',H_2O$, and may be regarded as a compound of water with a double molecule of ammonia $N_2H_6$, in which 2 atoms of $H$ are replaced by divalent platinum. This substance is also a base and forms salts, most of which are insoluble; the *platosamine sulphate* $N_2H_4Pt,H_2SO_4,Aq$ may be regarded as ammonium sulphate $(NH_4)_2SO_4$, in which 2 atoms of the hydrogen are replaced by platinum. The *platosamine hydrochloride* $N_2H_4Pt,2HCl$ is isomeric with the green salt of magnus, and may be obtained from that compound by dissolving in a hot solution of ammonium sulphate from which it crystallizes on cooling.

If the platosamine hydrochloride, suspended in boiling water, is treated with chlorine, it is converted into *platinamine hydrochloride* $N_2H_2Pt^{iv},4HCl$. The conversion of the

platosamine hydrochloride into platinamine hydrochloride may be shown by the following equation:

$$N_2H_4Pt,2HCl + Cl_2 = N_2H_2Pt,4HCl$$

By boiling the platinamine hydrochloride with silver nitrate, it is converted into *platinamine nitrate* $N_2H_2Pt(HNO_3)_4$; and when this is dissolved in boiling water and decomposed by ammonia, the *hydrated platinamine* $N_2H_2Pt,4H_2O$ is obtained in yellow prismatic crystals, having the same composition as that assigned to fulminating platinum (see Art. **199**).

**201.** Several other platinum compounds derived from ammonia have been obtained, but cannot at present be so conveniently classified. Table 4 shows the composition of those here enumerated, the platinum as it exists in platinous chloride $PtCl_2$ occupying the place of 2 atoms of hydrogen, being represented by $Pt''$; and platinum as it exists in platinic chloride $PtCl_4$ occupying the place of 4 atoms of hydrogen, by $Pt^{iv}$.

TABLE 4.

| | |
|---|---|
| Hydrated platosamine......... | $N_2H_4Pt'',H_2O$ |
| Platosamine hydrochloride..... | $N_2H_4Pt'',2HCl$ |
| Platosamine sulphate.......... | $N_2H_4Pt'',H_2SO_4,Aq$ |
| Hydrated platinamine......... | $N_2H_2Pt^{iv},4H_2O$ |
| Platinamine hydrochloride..... | $N_2H_2Pt^{iv},4HCl.$ |
| Hydrated diplatosamine....... | $N_4H_{10}Pt'',2H_2O$ |
| Diplatosamine hydrochloride... | $N_4H_{10}Pt'',2HCl,Aq$ |
| Diplatosamine sulphate....... | $N_4H_{10}Pt'',H_2SO_4$ |

Some of the salts of diplatinamine $N_4H_8Pt^{iv}$ have been obtained, this base being derived from 4 molecules of ammonia in which $H_4$ has been replaced by $Pt^{iv}$.

**202. Platinic Iodide.**—Platinic iodide $PtI_4$ is a dark-brown, amorphous substance which is soluble in $HI$, yielding a purple-red solution containing $2HI,PtI_4,9Aq$, which may be crystallized; hence the dark-red color when an acid solution of $PtCl_4$ is added to potassium iodide.

**203.** The **sulphides of platinum** correspond in composition with the oxides and chlorides, and may be obtained, by the action of hydrosulphuric acid on the respective chlorides, as black precipitates. $PtS_2$ combines with alkaline sulphides to form soluble compounds. $K_2S,3PtS,PtS_2$ is obtained by fusing spongy platinum with $KOH$ and sulphur.

**204.** **Platinum phosphide** $PtP_2$ and **platinum arsenide** $PtAs_2$ are lustrous, metallic bodies formed by direct combination at a high temperature.

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## PALLADIUM.

*Symbol Pd. Atomic weight 106.2. Valence II, IV, and VI.*

**205.** **Occurrence and Preparation.**—This metal is found in small quantity, associated with native gold and platinum. It closely resembles platinum in color as well as in general appearance, but is distinguished from it by being far more easily oxidized, and by its forming an insoluble cyanide. This circumstance is taken advantage of in separating palladium from platinum ores (see Art. **197**). The cyanide yields spongy palladium when heated, which may be fused in the same manner as platinum. When alloyed with native gold, palladium is separated by fusing the alloy with silver, and boiling it with nitric acid, which leaves the gold undissolved. The silver is precipitated from the solution as chloride, by adding sodium chloride, and metallic zinc is placed in the liquid, which precipitates the palladium, lead, and copper as a black powder. This is dissolved in nitric acid, and the solution mixed with an excess of ammonia, which precipitates the lead, leaving copper and palladium in solution. On adding hydrochloric acid in slight excess, a yellow precipitate of *palladamine hydrochloride* $N_2H_4Pd,2HCl$ is obtained, which leaves metallic palladium when heated.

**206. Properties.**—Palladium is malleable and ductile like platinum; its specific gravity, however, differs greatly from that metal, being only 11.4. Palladium is more oxidizable than platinum. When heated to redness in air, especially in the form of palladium sponge, it acquires a blue or purple superficial film of oxide, which is reduced at a white heat. Palladium is slowly attacked by nitric acid; its best solvent is nitromuriatic acid.

Palladium is remarkable for its power of occluding hydrogen. When heated to redness in a stream of that gas, it absorbs about 650 times its own volume of it. When brought in contact with nascent hydrogen, as when made to form the negative electrode in an electrolytic cell containing acidulated water, it can absorb over 900 times its volume of gas, whereby its specific gravity is reduced and its volume increased. Palladium black absorbs hydrogen more energetically than the compact variety. At 100°, 1 volume of it is said to absorb more than 980 volumes of the gas.

The absorption of the gas is attended with evolution of heat, and from this fact, together with the supposed constancy of composition of the hydrogenized palladium, it has been inferred that this product is a definite chemical compound; but this view can scarcely be regarded as satisfactorily demonstrated. If such a compound were formed, its formula would be $Pd_2H$.

Palladium, like platinum, forms two classes of compounds; namely, the palladious compounds, in which this metal is bivalent, and the palladic compounds, in which it is quadrivalent.

Palladium is useful, on account of its hardness, lightness, and resistance to tarnish, in the construction of philosophical instruments; alloyed with its own weight of silver, it is used for small weights.

Palladium compounds closely resemble those of platinum. Palladium forms three oxides, $Pd_2O$, $PdO$, and $PdO_2$; and two chlorides, $PdCl_2$ and $PdCl_4$. They are of little importance.

## RHODIUM.

*Symbol Rh. Atomic weight 103. Valence II, IV, and VI.*

**207. Occurrence, Preparation, and Properties.**—Rhodium is another of the metals associated with the ores of platinum. It is obtained from the solution of the ore in aqua regia by precipitating the platinum with ammonium chloride, neutralizing with sodium carbonate, adding mercuric cyanide to separate the palladium, and evaporating the filtered solution to dryness with excess of hydrochloric acid. On treating the residue with alcohol, the double chloride of rhodium and sodium is left undissolved, as a red powder. By heating this in a tube through which hydrogen is passed, the rhodium is reduced to the metallic state, and the sodium chloride may be washed out with water, leaving a gray powder of metallic rhodium, which is fused by the oxyhydrogen blowpipe at about 2,000°, and forms a hard metal of specific gravity 12.1. None of the acids, singly or conjoined, dissolves this metal, unless it is in the state of an alloy, as with platinum, in which state it is attacked by aqua regia. Rhodium may be brought into solution by fusing it with potassium bisulphate, when sulphur dioxide escapes, and a double sulphate of rhodium and potassium is formed, which gives a pink solution in water. When rhodium is melted with zinc and the alloy is boiled with an acid, the rhodium is left as a black powder, which is apparently an allotropic form of this metal.

**208.** Rhodium forms four oxides, namely, $RhO$, $RhO_2$, $RhO_3$, and $Rh_2O_3$, and one chloride, $RhCl_3$. With sulphur, rhodium combines energetically at high temperatures; two compounds, a monosulphide and a sesquisulphide, have been obtained.

An alloy of gold with between 30 and 40 per cent. of rhodium has been found in Mexico.

The compounds of rhodium are of minor importance in the arts or in practical chemistry.

## OSMIUM.

*Symbol Os. Atomic weight 190.3. Valence II, III, IV, and VIII.*

**209. Occurrence, Preparation, and Properties.**—Osmium occurs in the ores of platinum in flat scales, consisting of an alloy of osmium, iridium, ruthenium, and rhodium. This alloy also occurs occasionally associated with native gold, and, being very heavy, it accumulates at the bottom of the crucible in which the gold is melted. The osmium alloy is very hard and is frequently used for the points of gold pens. When the platinum ore is treated with aqua regia, this alloy is left undissolved. To extract the osmium from this residue, it is heated in a porcelain tube through which a current of dry air is passed, when the osmium is converted into perosmic anhydride, the vapor of which is carried forward by the current of air and condenses in bottles provided to receive it. The *perosmic anhydride* $OsO_4$ forms colorless prismatic crystals, which fuse and volatilize below the boiling point of water, yielding a most irritating vapor, which closely resembles chlorine. It is very soluble in water, giving a solution that exhales the same irritating odor and stains the skin black. Its acid properties are feeble, for it does not even redden litmus paper. Its solution in $HCl$ gives a black precipitate of $OsS_4$ with $H_2S$. By passing a mixture of $CO$ and vapor of $OsO_4$ through a red-hot porcelain tube, amorphous osmium is obtained, and may be converted into the crystalline form by fusing it with tin and dissolving in $HCl$, when blue, lustrous, cubical crystals of osmium are obtained, which are hard enough to scratch glass and which have a specific gravity of 22.48, thus being heavier than any other body.

By dissolving perosmic anhydride in potash, *potassium perosmate* is supposed to be formed, but this compound has not yet been isolated. When alcohol is added to this solution, the $OsO_4$ is apparently reduced to $OsO_3$, for rose-colored crystals of *potassium osmate* $K_2O, OsO_3, 2H_2O$ or $K_2OsO_4, 2H_2O$ are deposited; by treating this salt with

nitric acid, *osmic acid* $H_2OsO_4$ is obtained as a black powder, which has a tendency to oxidize in air, yielding an odor of perosmic anhydride.

When $OsO_4$ is dissolved in a solution of $SO_2$, *osmium sulphite* $OsSO_3$ is obtained. By adding an alkali to the solution, hydrated *osmium monoxide* $OsO, nH_2O$ is obtained as a bluish-black powder, which is easily oxidized and which dissolves in $HCl$ to a blue solution. $Os_2O_3$ and $OsO_2$ are obtained by heating *potassium osmochloride* $3KCl, OsCl_3$ and *osmichloride* $2KCl, OsCl_4$, respectively, with an alkali carbonate in absence of air.

**210. Osmium dichloride** $OsCl_2$ and **osmium tetrachloride** $OsCl_4$ are obtained as two distinct bodies when the metal is heated in chlorine; $OsCl_2$ is the less volatile, and forms green, needle-like crystals, while $OsCl_4$ is a dark-red powder. By mixing $Os$ with $KCl$, heating the mixture in chlorine, treating the mass with water, and evaporating, red octahedral crystals of $2KCl, OsCl_4$ separate, while from the mother liquor $3KCl, OsCl_3, 3H_2O$ is crystallized. When osmic acid is heated with $HCl$ and alcohol, and the solution is evaporated, crystals having the formula $Os_2Cl_7, 7H_2O$ are obtained, which are red when dry, but give a green solution when dissolved in water or in alcohol; by adding $KCl$ to the alcoholic solution, $K_2OsCl_6$ is precipitated, and when the filtrate is evaporated, $OsCl_3, 3H_2O$ crystallizes.

Several compounds of osmium salts with ammonia, called *osmamines*, are known, and a *potassium osmiamate* $KNOsO_3$ is obtained by the action of $NH_3$ on a solution of $OsO_4$ in $KOH$.

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## RUTHENIUM.

*Symbol Ru. Atomic weight 101.6. Valence II, IV, VI, and VIII.*

**211. Occurrence, Preparation, and Properties.**— Ruthenium was discovered in 1846 by Claus. It occurs chiefly in platinum ores, but has also been found in Borneo

in a mineral named *laurite*, which contains sulphides of ruthenium and osmium.

In the process of extracting osmium from the residue left on treating the platinum ore with aqua regia, by heating in a current of air, square, prismatic crystals of ***ruthenium dioxide*** $RuO_2$ are deposited nearer the heated part of the porcelain tube than the perosmic anhydride, for the dioxide is not itself volatile, being only carried forward mechanically. When $RuO_2$ is heated in $H$ the metal is obtained. It can be melted (1,800°) in the electric arc, and is then a gray and very hard metal; though brittle when cold, it becomes malleable when hot; it has a specific gravity of 12.06, and is insoluble in acids. When fused with zinc it yields an allotropic form similar to that described for rhodium.

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## COMPOUNDS OF RUTHENIUM.

**212.** When ruthenium is heated to 1,000° in oxygen, the volatile oxide $RuO_4$ is formed, and may be isolated by rapid cooling; but when the cooling process is allowed to proceed slowly, the compound decomposes again. This oxide may also be obtained by heating ruthenium with $KNO_3$ and $KOH$, and saturating the solution of the fused mass with chlorine, when $RuO_4$ sublimes. Ruthenium tetroxide is soluble in water, melts at 25.5°, and sublimes easily; at 107° it decomposes with explosion. It is also decomposed by light, yielding apparently $RuO_2$.

The oxides $RuO$ and $Ru_2O_3$ are probably also known. $RuCl_2$ and $RuCl_3$ are formed when the metal is heated in chlorine. The latter is insoluble in cold water, but dissolves in absolute alcohol to a purple-violet solution, which becomes indigo blue from absorption of water and formation of $RuCl_2OH$; the solution gradually deposits $Ru(OH)_3$. Double chlorides analogous to those of osmium exist.

Sulphates corresponding with $RuO$ and $Ru_2O_3$ have also been obtained.

## IRIDIUM.

*Symbol Ir. Atomic weight 193. Valence II, IV, and VI.*

**213. Occurrence, Preparation, and Properties.**—This metal obtained its name from *iris*, the rainbow, in allusion to the various colors of its compounds. It has been previously mentioned as occurring in the insoluble alloy from the platinum ores. It is sometimes found separately, and occasionally alloyed with platinum, the alloy crystallizing in octahedrons, which are heavier than platinum, having a specific gravity of 22.3. If the insoluble osmiridium alloy left by aqua regia is mixed with common salt and heated in a stream of chlorine, a mixture of sodio-chlorides of the metals is obtained and may be extracted by boiling water. If the solution is evaporated and distilled with nitric acid, the osmium is distilled off as perosmic anhydride, and by adding ammonium chloride to the residual solution, the iridium is precipitated as a dark red-brown ammonio-chloride, $2NH_4Cl, IrCl_4$ or $(NH_4)_2IrCl_6$, which leaves metallic iridium when heated. Like platinum, it then forms a gray, spongy mass, but is oxidized when heated in air, and may be fused at about 2,000° to a hard, brittle mass of specific gravity of 22.4, which does not oxidize in the air. Like rhodium, it is unattacked by aqua regia, unless alloyed with platinum. By fusion with zinc it yields an allotropic form, similar to that described for rhodium. The product of the oxidation of finely divided iridium in air is the *sesquioxide* $Ir_2O_3$, which is a black powder and insoluble in acids. The *monoxide* $IrO$ is also more easily acted on by alkalies than by acids; its solution in potash becomes blue when exposed to air, from the formation of the *dioxide* $IrO_2$. The *trioxide* $IrO_3$ is green. The *dichloride* $IrCl_2$ and *tetrachloride of iridium* $IrCl_4$ resemble the corresponding chlorides of platinum in forming double salts with the alkaline chlorides. There also exists a *trichloride of iridium* $IrCl_3$, whose solution has a green color, and gives a yellow precipitate with mercurous nitrate; and a blue precipitate, soon becoming white, however, with silver nitrate. Double compounds of

the chloride of ammonia (*iridamines*) are known. Iridium resembles palladium in its disposition to combine with carbon when heated in the flame of a spirit lamp.

Salts of iridium correspond with the oxides $IrO$ and $Ir_2O_3$.

An iridio-platinum alloy containing from 15 to 20 per cent. of iridium has been found very useful for making standard rules and weights, on account of its indestructibility, extreme rigidity, hardness, and high density.

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## GOLD.

*Symbol Au. Atomic weight 196.2. Valence I and III.*

**214. Occurrence and Preparation.**—Gold occurs quite widely distributed in nature, though in small quantity, as a rule. It is almost always found in the metallic state, usually associated, however, with certain quantities of silver, copper, or iron, and also in special ores, with bismuth and tellurium. Many minerals, such as galena, iron pyrites, and zinc blende, contain traces of gold. Though one of the rarest metals, it is widely distributed; the chief localities where it is mined being the Rocky Mountain and Pacific Coast states, in this country, Australia, South Africa, and the Klondike. It is found generally in quartz veins intersecting metamorphic rocks of various ages, and in the alluvial detritus (gravel) that has resulted from the disintegration of these rocks. Partly in consequence of the value of the metal, and partly from the simplicity of the methods by which it is worked, a deposit containing as little as 1 part of gold in 500,000 may sometimes be profitably worked. To extract gold from auriferous quartz, the whole is first powdered roughly by mechanical means, and then subjected to separation in sluices, so arranged that the heavier particles containing the gold collect at the bottom of the sluice, while the gangue is carried off by the stream of water. The gold is separated by causing it to form an amalgam with mercury, or to collect on amalgamated copper plates. The mercury is finally distilled off, leaving the gold behind as residue.

In the *chlorination process* the ore (iron pyrites) is roasted, so that the iron is transformed into ferric oxide, which is not readily attacked by moist chlorine, and then subjected to the action of chlorine. The gold is thus converted into chloride, which can be dissolved out in water, and metallic gold precipitated from the solution by the addition of reducing agents, such as ferrous sulphate.

Potassium cyanide is now largely used for extracting gold, as it readily dissolves in this reagent.

The separation of silver and copper from gold may be effected by *quartation*, the success of which, as the name implies, depends on the gold being present to the extent of not more than one-quarter of the mass of metal employed. The metal is boiled with strong sulphuric acid, and the silver and copper are thus converted into sulphates, so that on lixiviation with water these are dissolved and the gold left as a residue.

**215. Properties.**—Gold is a soft, orange-yellow metal of great brilliancy. Its physical character renders it very conspicuous among the metals; it is the heaviest of metals in common use, with the exception of platinum, its specific gravity being 19.33. In malleability and ductility it surpasses all other metals; the former property is turned to advantage for the manufacture of gold leaf, for which purpose a bar of gold, containing 96.25 per cent. of gold, 2.5 per cent. of silver, and 1.25 per cent. of copper, is passed between rollers, which extend it into the form of a broad ribbon; this is cut into squares, which are packed between layers of fine vellum, and beaten with a heavy hammer; these thinner squares are then again cut up and beaten between layers of gold-beater's skin until they are sufficiently thin. An ounce of gold may thus be spread over 100 square feet; 282,000 of such leaves placed upon each other form a pile of only 1 inch high. The gold leaves transmit green light, though when rendered non-lustrous by heat this light is ruby red.

The ductility of gold is exemplified in the manufacture of

gold thread for embroidery, in which a cylinder of silver, having been coated with gold leaf, is drawn through a wire-drawing plate and reduced to the thinness of a hair. Although fusing about the melting point of copper, gold is seldom cast, on account of its great contraction during solidification. Gold crystallizes in isometric forms, conducts heat and electricity well, and fuses at 1,035°. It is unaltered in air, and is not attacked by any single acid or alkali hydrate, though solutions containing free chlorine, like aqua regia, dissolve it readily.

Gold is used both for jewelry and coinage. Being too soft, alone, for either purpose, it is alloyed with copper or silver, the mint alloy of the United States consisting of 9 parts of gold and 1 part of copper. The purity of gold for jewelry is estimated by the *carat*, pure gold being 24 carats fine; hence an alloy of 18 parts of gold to 6 of silver and copper is said to be 18 carats fine.

**216. Gilding.**—Gold is not even affected to the same extent as silver by exposure to the atmosphere, for hydrogen sulphide has no action on it, and hence is better adapted than any other metal for coating surfaces that are required to preserve their luster.

Several processes are used for gilding metals, such as silver and copper. The objects may be gilded by amalgamation, or by galvanic deposition. Gold readily alloys with mercury, and the amalgam is used for gilding objects of silver and copper. The pieces to be gilded are heated, to destroy greasy matters, and are then cleaned by dipping them into dilute sulphuric acid, after which they are washed, and dried with sawdust. They are then rubbed with a brush of brass wires dipped into a solution of mercurous nitrate, and then with a brush impregnated with an amalgam of 1 part of gold and 8 parts of mercury. They are afterwards heated to volatilize the mercury. The pieces thus gilded are dull; they become lustrous after suitable washings and polishings.

The best process of gilding is the electrogilding. In this

process the copper objects, previously heated and cleaned by dilute sulphuric acid, are plunged for a few seconds in dilute nitric acid and then wiped dry. They are then connected with the negative pole of a battery and dipped into a bath composed of 1 part of cyanide of gold, 10 parts of potassium cyanide, and 100 parts of water. A plate of gold plunged into the same bath constitutes the positive pole. When the current passes, the objects become covered with a uniform and adherent coating of gold. As the metal is precipitated from the solution, it is replaced by an equivalent quantity from that which constitutes the positive pole, and which dissolves. The bath thus retains a constant composition.

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## COMPOUNDS OF GOLD.

**217. Oxides of Gold.**—Three compounds of gold and oxygen are so far known; namely, $Au_2O$, $AuO$, and $Au_2O_3$. They have, however, not yet found any practical importance in the arts.

*Aurous oxide* $Au_2O$, which is a violet-colored powder, is obtained by decomposing aurous chloride with potash. It is readily decomposed by hydrochloric acid, as shown by the subjoined equation:

$$3Au_2O + 6HCl = 2AuCl_3 + 3H_2O + 4Au$$

*Auric oxide* $Au_2O_3$ is obtained by gently heating *auric hydroxide* $Au(OH)_3$. This is prepared by heating a weak solution of auric chloride with excess of potash, and adding sodium sulphate, when auric hydroxide is precipitated. It is a very unstable compound, which evolves oxygen on exposure to light. It is soluble in nitric acid and in potassium hydrate; the latter solution yielding crystals of potassium aurate $KAuO_2, 3Aq$. By heating $Au(OH)_3$ at 160°, $AuO$ is formed.

**218. Chlorides of Gold.**—When precipitated gold is attacked by chlorine gas, it yields a dark-red, hard substance called *aurosoauric chloride*, having the formula $AuCl, AuCl_3$;

this is decomposed by water into two separate compounds, $AuCl$ and $AuCl_3$. The latter (*auric chloride*) may also be obtained by dissolving gold in hydrochloric acid with one-fourth of its volume of nitric acid, and evaporating on a water bath to a small bulk; on cooling, yellow prismatic crystals of a compound of auric chloride with hydrochloric acid, $AuCl_3,HCl,4Aq$, are deposited, from which the hydrochloric acid may be expelled by subjecting the compound to a slow heat not exceeding 120°, when the auric chloride forms red-brown, deliquescent crystals of $AuCl_3,2Aq$, dissolving very readily in water, giving a bright-yellow solution, which stains the skin and other organic matter purple when exposed to light, depositing finely divided gold. Almost every substance capable of combining with oxygen reduces the gold to the metallic state. The inside of a perfectly clean flask may readily be covered with a film of metallic gold by a dilute solution of auric chloride mixed with citric acid and ammonia, and gently heated. The facility with which it deposits metallic gold, and the resistance of the deposited metal to atmospheric action, has rendered auric chloride very useful in photography. Alcohol and ether readily dissolve auric chloride, the latter being able to extract it even from its aqueous solution. Red crystals of auric chloride are sublimed when thin gold foil is gently heated in a current of chlorine. Auric chloride forms crystallizable compounds with the alkaline chlorides and with the hydrochlorides of organic bases, and affords great help to the chemist in defining these last. *Aurochloride of sodium* forms reddish-yellow, prismatic crystals, $NaCl,AuCl_3,2Aq$, which are sold for photographic purposes.

*Aurous chloride* $AuCl$, also known as *protochloride of gold*, is obtained by subjecting auric chloride to a gentle heat, when it fuses, and at 177° decomposes, leaving the aurous chloride; continuing the heat, at about 200° the latter is reduced to metallic gold. Aurous chloride is sparingly soluble in water and has a pale color. Boiling water decomposes it into metallic gold and auric chloride.

*Fulminating gold* is obtained as a reddish-yellow precipitate

when ammonia is added to a solution of auric chloride; its composition is supposed to be $Au_2O_3,4NH_3$. It explodes violently when gently heated.

The *sel d'or* of the photographer is a *thiosulphate of gold and sodium* $Au_2S_2O_3,3Na_2S_2O_3,4Aq$, which is obtained in fine white needles by pouring a solution of 1 part of auric chloride into a solution of 3 parts of sodium thiosulphate, and adding alcohol, in which the double salt is insoluble. Its formation may be explained by the subjoined equation:

$$8Na_2S_2O_3 + 2AuCl_3$$
$$= Au_2S_2O_3,3Na_2S_2O_3 + 6NaCl + 2Na_2S_4O_6$$

It is, however, rather uncertain whether the above formula represents the true constitution of this salt, for it is not decomposed by acids in the same manner as ordinary thiosulphates are. Nitric acid causes the whole of the gold to separate in the metallic state.

*Purple of Cassius*, which is employed for imparting a rich red color to glass and porcelain, is a fine purple precipitate obtained by adding a solution of stannous chloride, containing stannic chloride, to auric chloride. Its composition is variable, but it consists essentially of gold associated with oxide of tin.

**219. Sulphides of Gold.**—Gold does not unite directly with sulphur, but by passing hydrogen sulphide through a solution of the double cyanide of gold and potassium $KCN,AuCN$, *aurous sulphide* $Au_2S$ is precipitated, and from a dilute solution of auric chloride the *disulphide* $Au_2S_2$ or a mixed sulphide $Au_2S,Au_2S_3$, is precipitated. The sulphides are soluble in alkaline sulphides, with which they form soluble double salts.

A SERIES

OF

# QUESTIONS AND EXAMPLES

Relating to the Subjects
Treated of in this Volume.

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It will be noticed that the pages of the Examination Questions that follow have been given the same section numbers as the Instruction Papers to which they refer. No attempt should be made to answer any of the questions or to solve any of the examples until the Instruction Paper having the same section number has been carefully studied.

# INORGANIC CHEMISTRY.

**(PART 1.)**

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## EXAMINATION QUESTIONS.

(1) State the chemical changes which occur in the leaden chambers in the manufacture of sulphuric acid.

(2) Define occlusion.

(3) How many grams of hydrogen must be burned to raise 50 kilograms of water from 0° to 10°?

(4) Why does a candle burn more brightly in oxygen than in air?

(5) By what tests could you prove that a substance which is stated to be sulphur, actually is that element?

(6) What do you understand by an *endothermic compound?*

(7) Complete the following equation: $2NaBr + Cl_2 = ?$

(8) Give a few simple tests by which you may be able to determine whether it is necessary to perform a more elaborate analysis of water or not.

(9) Mention some substances which contain hydrogen.

(10) What quantity of sulphuric acid and common salt must be taken to yield the following amounts of hydrochloric-acid gas: (*a*) 36.5 grams? (*b*) 1 kilogram?

$$\text{Ans.} \begin{cases} (a) & 49 \text{ gr. } H_2SO_4;\ 58.5 \text{ gr. } NaCl. \\ (b) & 1.3424 \text{ Kg. } H_2SO_4;\ 1.6027 \text{ Kg. } NaCl. \end{cases}$$

(11) What are the principal properties of chloric acid?

(12) In what compounds does chlorine occur in nature?

(13) How is sulphurous oxide prepared?

(14) Describe the chief properties of sulphur.

(15) Chlorine, bromine, and iodine are said to be members of one family of elements; make a comparison of their properties and of their chief compounds so as to show why they are so described.

(16) (*a*) Describe a method of obtaining hydrogen from water. (*b*) What weight of hydrogen is contained in 250 grams of water?

(17) Describe an experiment for proving that water is a compound body, and state precisely the conclusions to which the experiment leads you.

(18) How is sulphur commonly obtained?

(19) Illustrate by a rough sketch how you would collect a gas by *upward displacement.*

(20) What are the principal properties of hydrogen?

(21) What are the principal properties of hydrogen peroxide?

(22) (*a*) Does bromine occur free in nature? (*b*) In what form does it commonly occur in nature?

(23) Describe carefully the changes produced by raising the temperature of a piece of ice from $-10°$ to $150°$ C.

(24) How much oxygen can be obtained by heating 261 grams of manganese dioxide? Ans. 32 grams.

(25) What are the principal properties of hydrochloric acid?

(26) Give the reaction which takes place when zinc acts upon sulphuric acid.

(27) What do you understand by decrepitation?

(28) (*a*) How is hydrogen peroxide prepared? (*b*) What are the principal tests for it?

(29) (*a*) Describe two processes for the preparation of chlorine. (*b*) Give an equation and a sketch of the apparatus in each case.

(30) What do you understand by a desiccating agent?

(31) (*a*) State the principal properties of sulphurous oxide. (*b*) State the tests by which sulphurous oxide may be recognized.

(32) State the formula of selenic acid.

(33) From what does the name of hydrogen come?

(34) Wherein does nascent hydrogen differ, in its chemical behavior, from that element in the free state?

(35) Calculate the percentage composition of silver chloride $AgCl$. Ans. 24.739% of chlorine; 75.261% of silver.

(36) How much oxygen can be obtained by heat from 20 grams of mercuric oxide? Ans. 1.48 grams.

(37) Write the equation which expresses the preparation of hydrogen by the action of sodium on water.

(38) Show, through an equation, whether there will be any gas remaining if a mixture of 5 volumes of hydrogen and 3 volumes of oxygen are exploded by an electric spark.

(39) Translate into words the following equation: $2H_2O + K_2 = 2KOH + H_2$.

(40) Describe the properties of hypochlorous oxide obtained by passing dry chlorine gas over mercuric oxide, the reaction being represented by the following equation: $HgO + 2Cl_2 = HgCl_2 + Cl_2O$.

(41) How is bromine prepared?

(42) State the weight of 10 liters of tellurium vapor at 1,390°.

(43) Describe exactly how you would show the formation

of water from burning hydrogen, and sketch the apparatus you would use.

(44) What sulphur compounds occur in nature?

(45) Give the formula of Nordhausen sulphuric acid.

(46) Describe the method and the apparatus you would employ to verify the facts implied by the formula $HCl$.

(47) Ten liters of hydrogen are required; (*a*) how many grams of zinc; (*b*) how many grams of sulphuric acid would you need?

(48) What elements constitute the "Halogen Group"?

(49) (*a*) What are the resulting products when hydrogen, sulphur, and phosphorus are burned in oxygen? (*b*) Express the reactions by equations.

(50) Two aqueous solutions are given to you: one contains free bromine only, the other free iodine only; describe how you would prove the presence of the bromine in the one solution, and of the iodine in the other?

(51) Calculate the percentage composition of potassium chlorate.

(52) What volume is occupied by 32 grams of chlorine?
Ans. 10.094 liters.

(53) Express in words what is implied in the following equation: $Zn + H_2SO_4 = ZnSO_4 + H_2$.

(54) Name the oxides and acids of sulphur.

(55) You have given to you some red precipitate (mercuric oxide); state (*a*) whether you consider this substance to be a simple or a compound body; (*b*) whether it undergoes any chemical change when submitted to the action of heat; and if so, (*c*) what is the change and how it can be expressed symbolically?

(56) Describe how you would prepare *hydriodic acid.*

(57) What weight of sulphur is contained in 100 grams of hydrogen sulphide? Ans. 94.117 grams.

(58) Calculate the weight of 100 liters of hydrogen sulphide.

(59) (*a*) How is hydrofluoric acid prepared? (*b*) What is its action upon glass?

(60) What is the composition of water by weight, and how may it be experimentally determined?

(61) Give an account of the action of heat on sulphur.

(62) How does chlorine act as a bleaching agent?

(63) How would you prove by experiment that mercuric oxide is a compound and not an elementary body? Sketch and describe the apparatus you would use for this purpose.

(64) Hydrogen sulphide is passed into solutions of the following substances in different test tubes: *sodium arsenite*, and *antimony chloride*; what is the result in each instance?

(65) What is the percentage composition of hydrofluoric acid? Ans. 95% $F$; 5% $H$.

(66) State the principal properties of tellurium.

(67) How is hyposulphurous acid $H_2SO_2$ prepared?

(68) (*a*) Complete the following equation: $2NaI + MnO_2 + 2H_2SO_4 = ?$ (*b*) Express the same equation in words.

(69) Suppose you were requested to prepare some platinized asbestos for use in the laboratory; how would you proceed?

(70) (*a*) What is a unit of heat? (*b*) How many units of heat does hydrogen produce on combustion?

(71) State how sulphur may be converted into its various allotropic modifications.

(72) State what you understand by a *reducing agent*.

(73) State (*a*) the properties of sulphuric oxide; (*b*) its formula.

(74) (*a*) How would you prepare Schönbein's test paper? (*b*) For what purpose would you use it?

(75) What do you understand by the antiseptic or antizymotic property of a substance?

(76) (*a*) Name the materials and sketch the apparatus required for the production of hydrochloric acid. (*b*) Explain, by means of an equation, the chemical change in which this acid is produced.

(77) (*a*) Give a short account of the history of sulphuric acid. (*b*) State whether you consider it an important compound in the laboratory and the arts, and, if so, why.

(78) What do you understand by *metalepsis?*

(79) What are the principal properties of oxygen?

(80) If you were told to prepare a freezing mixture, how would you proceed and what substances do you need?

(81) How is hydrogen sulphide prepared?

(82) What takes place when electric sparks are passed through dry oxygen?

(83) Give some account (*a*) of the chief properties of bromine, and (*b*) of the tests by which it may be recognized.

(84) Give a description of Carré's ice-producing machine, and explain how it works and the chemical principles involved.

(85) How is sulphuric acid detected?

(86) How could you prove that sulphur was a constituent of hydrogen sulphide?

(87) What do you understand by an allotropic form of oxygen? How is this substance distinguished from ordinary oxygen?

(88) What is disulphuric acid, and how is it made?

(89) Ten grams of $S$ give how many grams of $SO_2$?

# INORGANIC CHEMISTRY.

(PART 2.)

## EXAMINATION QUESTIONS.

(1) Complete the following equation, and give the names of the factors and the products:

$$3CaF_2 + B_2O_3 + 3H_2SO_4 = 3CaSO_4 + ? + ?$$

(2) Required, 594 grams of carbon dioxide. (*a*) How will you obtain it? (*b*) What weight of calcium carbonate do you require?

(3) Name the constituents of the atmosphere.

(4) A substance having a molecular weight of 108 is found to contain, on analysis, 74.07 per cent. of oxygen and 25.93 per cent. of nitrogen. (*a*) Calculate from these data its formula. (*b*) Give the name of the compound.

(5) How many kilograms of calcium are in 1,000 kilograms of calcium carbonate?

(6) State the chief properties of carbon disulphide.

(7) What is the percentage composition of ammonia?

$$\text{Ans.} \begin{cases} N, \ 82.353\%. \\ H, \ 17.647\%. \end{cases}$$

(8) In what way may nitrogen be prepared?

(9) Suppose some one shows you a glass jar filled with a colorless gas, whose specific gravity has been ascertained to be 1.806 and its density to be 25.98; it possesses a strong odor of bitter almonds. Would you be able to name the gas from these properties?

(10) State the chief properties of carbon monoxide.

(11) Give the formula for Scheele's green.

(12) Give the chemical stages in making phosphorus.

(13) Two hundred and fifty c. c. of nitrogen, at ordinary temperature and pressure, weigh how much? Ans. .31375 g.

(14) State how you would ascertain the composition of marsh gas (*a*) by volume; (*b*) by weight.

(15) State by an equation the reaction that occurs when silicon chloride is brought in contact with water.

(16) What reasons are there for believing that air is a mechanical mixture, and not a chemical combination of oxygen and nitrogen?

(17) Give the formula for hydroxylamine.

(18) Give the names of the following compounds: $H_2NaPO_4$, $HCaPO_4$, $BiPO_4$.

(19) Give the formulas of (*a*) arsenate of soda; (*b*) calcium arsenate.

(20) Describe the process of making coal gas.

(21) Give a short account of the structure of a flame.

(22) How much sulphur must be transformed into vapor to yield 76 grams of carbon disulphide? Ans. 64 g.

(23) What is the percentage composition of borax?

$$\text{Ans.} \begin{cases} Na, & 22.77\%. \\ B, & 21.78\%. \\ O, & 55.45\%. \end{cases}$$

(24) Name and give the properties of the compounds formed according to the following equation:

$$4H_3PO_3 = 3H_3PO_4 + PH_3$$

(25) You are called on to weigh out sufficient copper and nitric acid to produce 100 liters of nitrogen dioxide at 0° and 760 mm. pressure. What weight in grams of copper and nitric acid would you take?

$$\text{Ans.} \begin{cases} Cu, & 418.95 \text{ g.} \\ HNO_3, & 1,117.2 \text{ g.} \end{cases}$$

(26) Explain the use made by jewelers and others of the touchstone.

(27) (*a*) Describe Marsh's test. (*b*) What is the limit of its delicacy?

(28) Mention the forms in which carbon occurs in nature.

(29) Give a short description of Schrötter's carbon-dioxide apparatus and the principles on which it is based.

(30) (*a*) How is methane produced naturally? (*b*) How is it prepared artificially?

(31) Define combustion.

(32) How is cyanogen gas prepared?

(33) How much carbon dioxide is furnished by burning 48 grams of carbon? Ans. 176 g.

(34) Describe how the specific gravity of an ammonia solution is obtained by means of the pycnometer.

(35) Describe the principles of Carré's freezing machine.

(36) Why does a candle burn more brightly in oxygen than in air?

(37) Give the properties of arsenious oxide.

(38) Air contains 23 per cent. of its weight of oxygen; how many grams of phosphorus are needed to burn out the whole of the oxygen in 100 grams of air when the highest oxide of phosphorus is formed?

(39) Finish the following equation:

$$CO_2 + H_2O = ?$$

(40) Show through an equation the changes that occur when carbon monoxide is passed over red-hot copper oxide.

(41) How many cubic meters of oxygen are required for the complete combustion of 1,000 kilograms of carbon?

Ans. 1,866.06 cu. m.

(42) How many grams of quicklime are necessary to prepare 59 grams of ammonia?

(43) What is the percentage composition of ethylene gas?

Ans. $\begin{cases} H, 14.28\%. \\ C, 85.72\%. \end{cases}$

(44) Describe the construction of a Bunsen burner.

(45) Give the method of preparation and the properties of silicon.

(46) Finish the following equation:

$$Si + 3HCl = ?$$

(47) How many liters of ammonia are absorbed by 3.92 liters of water (*a*) at 0° C.? (*b*) at 15° C.?

(48) One kilogram of zinc gives what volume of $N_2O$ with nitric acid? Ans. 85.787 l.

(49) How would you prepare a nitrate from nitric acid?

(50) How do common and allotropic phosphorus differ?

(51) What are the best antidotes in case of arsenic poisoning?

(52) How can you account for the deodorizing property of charcoal?

(53) Find the volume in liters of the carbon monoxide obtained from 100 grams of oxalic acid. Ans. 24.88 l.

(54) How does silicon occur in nature?

(55) How much nitric acid is obtained from 170 grams of sodium nitrate? Ans. 126 g.

(56) Two hundred and fifty c. c. of ammonia decomposed by electric sparks give what volume of mixed gases?

(57) What weight of phosphorus pentoxide can be obtained by burning 793 grams of phosphorus in oxygen?

Ans. 1,816.22 g.

(58) (*a*) State the properties of aqua regia. (*b*) How many measured cubic centimeters of each of its constituents would you use to prepare 1 liter of aqua regia?

(59) Give the preparation and properties of phosphoric acid.

(60) How can you account for the striking difference in the properties of diamond, graphite, and charcoal?

(61) Is carbonic acid $H_2CO_3$ a dibasic acid; if so, why?

(62) Explain the principles of the Davy safety lamp.

(63) How is silicon chloride prepared?

(64) Ten grams of hydrochloric acid $HCl$ act on zinc, and the same weight of acid acts on calcium carbonate; what bulk of gas, measured at the normal temperature and pressure, is produced in each case?

The following equations represent the chemical changes:

$$2HCl + Zn = ZnCl_2 + H_2$$
$$2HCl + CaCO_3 = CaCl_2 + H_2O + CO_2$$

(65) Give a short account of how the determination of the composition of $HNO_3$ is effected.

(66) Give the properties of metallic, or steel-gray, arsenic.

(67) How is olefiant gas prepared?

(68) How could you ascertain whether the air of a room is contaminated with too much carbon dioxide?

(69) You need, for a certain experiment, 50 grams of cyanogen; how many grams of cyanide of mercury would you require to prepare the above mentioned quantity?

Ans. 242.308 g.

(70) Give the composition by weight and the formulas of the five oxides of nitrogen.

(71) (*a*) Give the formula of phosphine. (*b*) Describe its preparation. (*c*) Show the occurring reaction by an equation.

(72) In preparing nitrogen dioxide, would you consider it advisable to connect the delivery tube with long rubber joints?

(73) A heavy, white powder, supposed to be arsenious oxide, is given to you. How can you, without making an elaborate chemical analysis, make sure that this powder is really arsenious oxide?

(74) How much pure air ought to be mixed with 100 measures of firedamp (marsh gas) in a coal mine, in order to supply material for the complete combustion of marsh gas during explosion? (Pure air contains 21 per cent. of $O$.)

The combustion of marsh gas is represented by the following equation:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

(75) (*a*) How is acetylene produced? (*b*) What are its properties?

(76) How much sulphur is required to prepare 1.25 liters of carbon-disulphide vapor? Ans. 3.578 g.

(77) State what special use is made of hyponitrous oxide.

(78) How is arsenic separated from its ores?

(79) What volume of methane would you be able to obtain from 888 grams of sodium acetate?

(80) If you shake some lime water with carbon dioxide, the clear lime water becomes milky. Does that also occur when, instead of the carbon dioxide, carbon monoxide is employed?

(81) Give the formula of potassium hypophosphite.

(82) (*a*) What do you understand by dialysis? (*b*) State how you would proceed if you were told to dialyze a substance.

(83) Fifteen grams of ammonium nitrate yield what volume of $N_2O$?

(84) How is $COS$ prepared?

(85) (*a*) What do you understand by hard and soft water? (*b*) What causes the hardness of water? (*c*) Can the hardness of water be removed?

(86) Is carbon dioxide poisonous by itself; if not, why, then, is it dangerous to human life when inhaled in even moderate quantities?

(87) State how you would prove the presence of arsenite of copper in a bright green-colored piece of wall paper.

(88) How can ammonia be liquefied?

(89) Where do animals get the phosphorus they need?

(90) Give the names and formulas of the sulphides of arsenic.

(91) (*a*) How does silica occur in nature? (*b*) Give its formula.

(92) Name the oxides of arsenic.

(93) How is trihydrogen phosphate prepared?

(94) How may we determine the composition of the air by weight, as regards nitrogen and oxygen?

# INORGANIC CHEMISTRY.

(PART 3.)

## EXAMINATION QUESTIONS.

(1) Give the formula of scandia.

(2) If the following formula be made the basis of the soda process, (*a*) how much soda will 71 kilograms of sodium sulphate yield? (*b*) 426 kilograms?

$$(1) \qquad Na_2SO_4 + C_2 = Na_2S + 2CO_2$$
$$(2) \qquad Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

(3) State Richter's law concerning the general composition of salts.

(4) State the law of multiple proportions.

(5) What is so called *galvanized iron?*

(6) Complete the following equation, and name the factors and products:

$$CaC_2 + 2H_2O = ?$$

(7) Give the formula of slaked lime.

(8) A saturated solution of sodium chloride boils at what temperature?

(9) What do you understand by a gram molecule?

(10) The mineral cryolite has the formula $Na_3AlF_6$; what percentage of aluminum does it contain?

Ans. 13.064%.

(11) State the general chemical properties of the metallic oxides.

(12) A line of what color and wave length characterizes the spectrum of lithium?

(13) State what you know about the composition of metallic sulphates.

(14) How much calcium carbide is required to produce 29 liters of acetylene gas? Ans. 82.806 g.

(15) What is *permanent white*, or *blanc fixe*, employed by painters, etc.?

(16) State what you know about the properties, physical, as well as chemical, of the metals.

(17) State what you know about the manufacture of potassium, and give its general properties.

(18) Are metallic carbonates, as a rule, soluble in pure water?

(19) State the law of constant proportions.

(20) Calculate the percentage composition of sodium carbonate.

(21) Give the formula of ammonium bicarbonate.

(22) What is the valence of barium?

(23) What do you understand by atomic volume, and how is the atomic volume of an element obtained?

(24) Show, by equation, the resulting products obtained by the action of chlorine upon a concentrated solution of potassium hydrate.

(25) Give the process adopted by *Morin* for preparing aluminum.

(26) State the law of reciprocal proportions.

(27) Give symbol, atomic weight, and valence of indium.

(28) How does barium occur in nature?

(29) Define oxy-acids.

(30) Give the formula of magnesia.

(31) How much lime may be obtained from 139 kilograms of calcium carbonate? Ans. 77.84 Kg.

(32) (*a*) Give the theory of ammonium. (*b*) Illustrate it.

(33) What do you understand by the *chemical equivalent* of an element?

(34) Give the formula of gallium sesquioxide.

(35) Give symbol, atomic weight, and properties of lithium.

(36) It is stated, in Art. **39,** that *the properties of the elements are periodic functions of their atomic weights.* (*a*) Explain why these properties are called "periodic." (*b*) Who were the discoverers of these functions?

(37) Show, by an equation, the formation of hydro-potassium tartrate.

(38) (*a*) What is an alloy? (*b*) What is an amalgam?

(39) If zinc blende and smithsonite are pure, what percentage of zinc ought each of these metals to yield, assuming that there is no loss? Ans. $\begin{cases}\text{Zinc blende, 67\%.}\\\text{Smithsonite, 52\%.}\end{cases}$

(40) Write the formula of aluminum chloride.

(41) Who conceived the idea of the existence of molecules?

(42) Give the origin of the name cæsium.

(43) What is "philosopher's wool"?

(44) Are metallic nitrates soluble in water?

(45) (*a*) Which contains the larger percentage of oxygen—strontianite or witherite? (*b*) What percentage of oxygen does each contain?

(46) Give the composition (*a*) of American gold coins, (*b*) of aluminum bronze, and (*c*) of Britannia metal.

(47) Define hydracids.

(48) State (*a*) the preparation and (*b*) the properties of sodium.

(49) What amount of potassium hydrate will 69 kilograms of potassium carbonate yield? Ans. 56 Kg.

(50) State what you know about the history and occurrence of zinc.

(51) How much calcium hydrate may be obtained from 250 kilograms of lime? Ans. 330.357 Kg.

(52) Who discovered rubidium?

(53) State how the vapor density of a substance that is gaseous at ordinary temperature is obtained.

(54) Under what names does aluminum oxide occur in nature?

(55) (*a*) What were the new elements whose existence and properties were predicted by Mendeléeff? (*b*) By what names did he call them?

(56) Give the formula of ammonium nitrate.

(57) Give the formula of magnesia alba.

(58) Are all metallic sulphates soluble in water? If not, state the names of the metals that form insoluble or, perhaps, only slightly soluble sulphates.

(59) (*a*) How is baryta obtained? (*b*) Give its formula and general properties.

(60) What is the percentage composition of common salt?

$$\text{Ans.} \begin{cases} Na, & 39.32\%. \\ Cl, & 60.68\%. \end{cases}$$

(61) Are metallic sulphides attacked by chlorine?

(62) State some of the characteristic properties of metallic nitrates.

(63) What are atomic analogues?

(64) Give the formula of *Epsom salt*.

(65) What is the chief use of anhydrous calcium chloride in the laboratory?

(66) What is the percentage composition of borax?

(67) The mineral fibrolite contains 36.8 per cent. of silicic oxide, and 63.2 per cent. of aluminum oxide; its molecular weight is 163. What is its formula?

(68) Describe *Victor Meyer's apparatus*, and state for what purpose the same is used.

(69) Define the meaning of *neutral*, *acid*, and *basic salts*.

(70) Give symbol, atomic weight, and valence of calcium.

(71) Find the formula and give the name of a salt having the following percentage composition, and a molecular weight of 246: magnesium, 9.76 per cent.; sulphur, 13.01 per cent.; oxygen, 26.01 per cent.; water, 51.22 per cent.

(72) State the properties and give the formula of potassium sulphate.

(73) Name a metal which eagerly absorbs dry oxygen at ordinary temperatures.

(74) Mention some of the characteristic features of the metallic sulphates.

(75) What do you understand by the molecular volume of a compound?

(76) State who discovered the element cæsium.

(77) In what compounds does aluminum occur in nature?

(78) What do you understand by *haloid salts?*

(79) Give the formula of barium peroxide.

(80) How much chlorine with potassium hydrate is necessary to yield the following quantities of potassium chlorate: (*a*) 336 kilograms? (*b*) 200 grams?

Ans. { (*a*) 584.23 Kg.
(*b*) 347.76 g.

(81) How was rubidium detected and its name derived?

(82) How is plaster of Paris obtained?

(83) State what you know about Preston salt, how it is prepared, etc.

(84) State the names of the metals whose sulphides are soluble in water.

(85) Name the chief compounds of cadmium.

(86) Give the composition of the different oxides formed by the metals.

(87) By whom and when was potassium discovered?

(88) Give the percentage composition of barium chlorate.

(89) (*a*) How is caustic potash prepared? (*b*) Give its formula and properties.

# INORGANIC CHEMISTRY.

(PART 4.)

(1) Give the formula of niobic acid.

(2) How does gold occur in nature?

(3) Mention some of the most important physical properties of iron.

(4) What percentage of nickel does niccolite contain?
Ans. 43.90%.

(5) What volume of chlorine, at normal temperature and pressure, is contained in 1 gram of stannous chloride?
Ans. .1185 l., or 118.5 c. c.

(6) Mention the properties of metallic copper.

(7) How is mercurous iodide prepared?

(8) How much cobaltous oxide is required to yield 36 grams of cobaltous nitrate? Ans. 14.69 g.

(9) (*a*) What amount of potassium dichromate and sulphuric acid is necessary to yield 998 grams of chrome alum? (*b*) How much water will be formed during its preparation?

(10) Mention the name of the mineral in which silver chloride occurs in nature.

(11) What is the composition of red hematite?

(12) What per cent. of silver does silver nitrate contain?
Ans. 63.53%.

(13) Give the formula of cobalto-cobaltic oxide.

(14) Mention the properties of palladium.

(15) By what chemical process is nickel obtained?

(16) Give the formula of germanium tetrachloride.

(17) Give the formula of (*a*) chromate of potash; (*b*) chromate of lead; (*c*) anhydrochromate of potash.

(18) How is *Salzburg vitriol* prepared?

(19) How is ferrous sulphate prepared?

(20) State the preparation and properties of uranium.

(21) How is white lead prepared?

(22) If chromic oxide is obtained by the reaction

$$K_2Cr_2O_7 + C_2 = Cr_2O_3 + K_2CO_3 + CO$$

how much $Cr_2O_3$ will 853 grams of $K_2Cr_2O_7$ yield?

Ans. 442.4 g.

(23) What per cent. of iron, theoretically, do the following three ores contain: (*a*) red hematite? (*b*) iron pyrites? (*c*) magnetic iron ore?

(24) What weight of copper may be obtained from 1,000 kilograms of malachite? Ans. 572.73 Kg.

(25) One gram of $PtCl_4$ contains what volume of chlorine gas? Ans. 132.176 c. c.

(26) In what form does tin occur in nature?

(27) How does chromium occur in nature?

(28) From how much black oxide of manganese and hydrochloric acid must the chlorine be evolved to change 118 grams of tin into stannic chloride? Ans. $\begin{cases} HCl, 292 \text{ g.} \\ MnO_2, 174 \text{ g.} \end{cases}$

(29) Name the metals which belong to the bismuth group of metals.

(30) Give the formula of cupric sulphate.

(31) An alloy of platinum and gold has a specific gravity of 20; what per cent. of platinum does it contain?

Ans. 30.87%.

(32) Give the formula of ammonium metavanadate.

(33) Give the formula of the compound usually known as "cobalt bloom."

(34) What are the objections to the use of lead water pipes?

(35) How does molybdenum occur in nature?

(36) Mention some of the characteristics of cobalt.

(37) How much mercuric sulphate and how much salt is required to yield 500 grams of $HgCl_2$?

Ans. $\begin{cases} HgSO_4, \ 546.1 \text{ g.} \\ NaCl, \ 215.9 \text{ g.} \end{cases}$

(38) State how "Thenard's blue" is prepared.

(39) To which family group of metals does uranium belong?

(40) In what form does titanium occur in nature?

(41) Calculate the percentage composition of manganous sulphide.

(42) Give the chemistry of the various processes of making steel.

(43) Give the formula of molybdenite.

(44) Give the formulas of the oxides of tantalum.

(45) Give the formula (*a*) of mercurous sulphate; (*b*) of mercuric sulphate.

(46) To prepare 962 grams of stannic chloride, how much tin is necessary? Ans. 436.6 g.

(47) How does tungsten occur in nature?

(48) If 250 grams of pure iron are burned in an excess of chlorine, (*a*) what compound is formed? (*b*) How much of it?

(49) Name the compounds that have the following formulas: (*a*) $Tl(OH)_3$; (*b*) $Tl_2S_3$; (*c*) $TlCl$.

(50) Give the formula of molybdenum pentachloride.

(51) Give the formula of tungsten trioxide.

(52) Calculate the percentage of antimony in antimonious sulphide. Ans. 71.43%.

(53) How is the name "chromium" derived?

(54) State the different methods by which platinum is refined.

(55) What volume of $SO_2$, at normal temperature and pressure, will 1,000 kilograms of galenite yield?
Ans. 93,650.66 l.

(56) Calculate the percentage composition of $Hg_2O$.
Ans. $\begin{cases} Hg, & 96.15\%. \\ O, & 3.85\%. \end{cases}$

(57) With what other elements is platinum usually associated in nature?

(58) How are the two chlorides of antimony prepared?

(59) Give the formula of sodium zirconate.

(60) What remarkable property distinguishes platinum black?

(61) Describe the principles of "Döbereiner's lamp."

(62) How much silver is required to prepare 250 grams of silver nitrate? Ans. 158.82 g.

(63) Give the formulas of the four different oxides formed by rhodium.

(64) Give the formulas of oxides formed by cerium.

(65) Mention the minerals in which lead chiefly occurs.

(66) Give the formulas and names of the various manganese oxides.

(67) (*a*) How is silver bromide obtained? (*b*) State its properties.

(68) Write the chemical reactions that take place in obtaining lead from galena.

(69) What weight of potassium permanganate may be obtained from 1,010 grams of $MnO_2$? The reaction is

$$2MnO_2 + 3O + K_2O = K_2Mn_2O_8$$

Ans. 1,834.25 g.

(70) How is $Ag_2SO_4$ obtained?

(71) Give the names of the principal minerals in which titanium occurs.

(72) Give the formulas of the oxides of gold.

(73) If a platinum vessel weighs 392 grams, what would be its weight if made of nickel? Ans. 156.8 g.

(74) Give the formula and the properties of nickel carbonyl.

(75) What valence has chromium in its oxides?

# A KEY

TO ALL THE

## QUESTIONS AND EXAMPLES

CONTAINED IN THE

## EXAMINATION QUESTIONS

INCLUDED IN THIS VOLUME.

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The Keys that follow have been divided into sections corresponding to the Examination Questions to which they refer, and have been given corresponding section numbers. The answers and solutions have been numbered to correspond with the questions. When the answer to a question involves a repetition of statements given in the Instruction Paper, the reader has been referred to a numbered article, the reading of which will enable him to answer the question himself.

To be of the greatest benefit, the Keys should be used sparingly. They should be used much in the same manner as a pupil would go to a teacher for instruction with regard to answering some example he was unable to solve. If used in this manner, the Keys will be of great help and assistance to the student, and will be a source of encouragement to him in studying the various papers composing the Course.

# INORGANIC CHEMISTRY.

(PART 1.)

(1) See Art. **125.**

(2) See Art. **4.**

(3) 1 kilogram = 1,000 grams; 50 kilograms = 50,000 grams. See Art. **5.** 1 gram of burning hydrogen raises 34,462 grams of water from 0° to 1°. Then, 50,000 ÷ 34,462 = 1.45 grams of hydrogen are needed to raise 50,000 grams from 0° to 1°, and 1.45 × 10, or 14.5, grams will be required to raise the same quantity of water to 10°. Ans.

(4) See Art. **11.** Oxygen is an extremely active supporter of combustion, while air, being composed of oxygen and nitrogen, the latter of which is not a supporter of combustion, is a less active supporter.

(5) See Art. **100.**

(6) See Art. **61.**

(7) $2NaBr + Cl_2 = 2NaCl + Br_2$.

(8) See Art. **36.**

(9) All acids, all hydrates, organic compounds, such as alcohol, petroleum, etc. See Art. **2.**

(10) Hydrochloric-acid gas is prepared according to the equation

$$\underset{98}{H_2SO_4} + \underset{117}{2NaCl} = \underset{73}{2HCl} + \underset{142}{Na_2SO_4}$$

Then,

(*a*) $73 : 98 = 36.5 : 49$ grams $H_2SO_4$;
$73 : 117 = 36.5 : 58.5$ grams $NaCl$.

(*b*) $73 : 98 = 1 : 1.3424$ kilograms $H_2SO_4$;
$73 : 117 = 1 : 1.6027$ kilograms $NaCl$. Ans.

(11) See Art. **71.**

(12) See Art. **44.**

(13) See Art. **115.**

(14) See Art. **99.**

(15) See Art. **85.**

(16) (*a*) See Art. **3** and Art. **31,** Experiment 22.

(*b*) A molecule of water contains 2 parts of hydrogen and 16 parts of oxygen, or 1 gram of water contains $\frac{2}{18}$ or $\frac{1}{9}$ part of its weight of hydrogen:

$$250 \div 9 = 27.777+ \text{ grams of } H. \quad \text{Ans.}$$

(17) See Arts. **30** and **31.**

(18) See Art. **98.**

(19) See Fig. 13 and Art. **22.**

(20) See Arts. **4** and **5.**

(21) See Art. **40.**

(22) (*a*) No.

(*b*) See Art. **75.**

(23) See Art. **28.**

(24) See Art. **10.** Oxygen is prepared according to the equation

$$\underset{261}{3MnO_2} = \underset{229}{Mn_3O_4} + \underset{32}{O_2}$$

Then,

$$261 : 32 = 261 : 32 \text{ grams.} \quad \text{Ans.}$$

(25) See Art. **55.**

(26) $H_2SO_4 + Zn = ZnSO_4 + H_2$. See Art. **3.**

(27) See Art. **10.**

(28) (*a*) See Art. **39.**
(*b*) See Art. **41.**

(29) (*a*) See Art. **45.**
(*b*) See Figs. 23 and 24.

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$$
$$2NaCl + 2H_2SO_4 + MnO_2 = MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2$$

(30) A desiccating agent is a compound that possesses a strong affinity for water or moisture; as, for instance, sulphuric acid, calcium chloride, etc. See also Art. **5.**

(31) (*a*) See Art. **116.**
(*b*) See Art. **117.**

(32) $H_2SeO_4$. See Art. **139.**

(33) See Art. **5.**

(34) Nascent hydrogen is distinguished by its increased chemical activity. See Art. **108,** *Theoretical Chemistry.*

(35) Silver has an atomic weight of 108; chlorine has an atomic weight of 35.5. Molecular weight of $AgCl$ = 143.5. Using formula **1,** *Theoretical Chemistry,*

$$x = \frac{100an}{m},$$

and substituting the given values, we obtain

$$x = \frac{100 \times 108 \times 1}{143.5} = 75.261\% \text{ of silver,}$$

$$x = \frac{100 \times 35.5 \times 1}{143.5} = 24.739\% \text{ of chlorine. Ans.}$$

(36) See Art. **10.** The production of oxygen from mercuric oxide is expressed by the equation

$$\underset{431.6}{2HgO} = \underset{399.6}{2Hg} + \underset{32}{O_2}$$

Then,

431.6 : 32 = 20 : 1.48 grams of oxygen. Ans.

(37) $2Na + 2H_2O = 2NaHO + H_2$. See Art. **3.**

(38) $5H_2 + 3O_2 = 5H_2O + O.$

(39) Two molecules of water and 1 molecule of potassium yield 2 molecules of potassium hydrate and 1 molecule of hydrogen.

(40) See Art. **61.**

(41) See Art. **76.**

(42) 114.7 grams.

(43) See Art. **5.**

(44) See Art. **97.**

(45) $H_2S_2O_7$.

(46) See Art. **56.**

(47) Hydrogen is obtained according to the equation

$$\underset{98}{H_2SO_4} + \underset{65}{Zn} = \underset{161}{ZnSO_4} + \underset{2}{H_2}$$

10 liters of hydrogen weigh .896 gram; then,

2 : 65 = .896 : 29.120 grams of zinc,

2 : 98 = .896 : 43.904 grams of sulphuric acid. Ans.

(48) Chlorine, bromine, iodine, and fluorine. See Art. **73.**

(49) (*a*) Water, sulphur dioxide, phosphorus pentoxide.

(*b*)

$$\begin{aligned} 2H_2 + O_2 &= 2H_2O \\ S + O_2 &= SO_2 \\ P_4 + 5O_2 &= 2P_2O_5 \end{aligned}$$

(50) Bromine colors a solution of starch yellow, while iodine gives a blue color to the solution. See also Arts. **77** and **80.**

(51) Potassium chlorate has the formula $KClO_3$; its molecular weight is 122.5. Using formula **1,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

and substituting the known values, we obtain

$$x = \frac{100 \times 39 \times 1}{122.5} = 31.84\% \ K,$$

$$x = \frac{100 \times 35.5 \times 1}{122.5} = 28.98\% \ Cl,$$

$$x = \frac{100 \times 16 \times 3}{122.5} = 39.18\% \ O. \quad \text{Ans.}$$

(52) 3.17 grams occupy the volume of 1 liter. 1 gram occupies, then, the volume of .31545 liter, and 32 grams will occupy 10.094 liters. Ans.

(53) One molecule of zinc and 1 molecule of sulphuric acid yield 1 molecule of zinc sulphate and 1 molecule of hydrogen.

(54)

| | | | |
|---|---|---|---|
| Hyposulphurous oxide | $S''O$ | Hyposulphurous acid | $H_2S''O_2$ |
| Sulphurous oxide | $S^{iv}O_2$ | Sulphurous acid | $H_2S^{iv}O_3$ |
| Sulphuric oxide | $S^{vi}O_3$ | Sulphuric acid | $H_2S^{vi}O_4$ |

(55) See Art. **10.**

(56) See Art. **88.**

(57) Hydrogen sulphide has the formula $H_2S$; its molecular weight is 34. Using formula **10,** *Theoretical Chemistry*,

$$w = \frac{Wm}{M},$$

and substituting the known values, we obtain

$$w = \frac{100 \times 32}{34} = 94.117 \text{ grams.} \quad \text{Ans.}$$

(58) 1 liter of $H_2S$ weighs 1.52 grams, 100 liters weigh 152 grams.

(59) (*a*) and (*b*) See Art. **90.**

(60) 16 parts, by weight, of oxygen,
2 parts, by weight, of hydrogen.

For the determination of the composition of water by weight, see Art. **34.**

(61) See Art. **99.**

(62) See Art. **48.**

(63) See Art. **10,** Experiment 7, and Figs. 6 and 7.

(64) See Art. **108.**

(65) Hydrofluoric acid has the formula $HF$ and a molecular weight of 20. Using formula **1,** *Theoretical Chemistry*,

$$x = \frac{100\,a\,n}{m},$$

and substituting the known values, we obtain:

$$x = \frac{100 \times 1 \times 1}{20} = 5\% \text{ of } H,$$

$$x = \frac{100 \times 19 \times 1}{20} = 95\% \text{ of } F. \quad \text{Ans.}$$

(66) See Art. **145.**

(67) See Art. **113.**

(68) (*a*) $2NaI + MnO_2 + 2H_2SO_4$
$= Na_2SO_4 + MnSO_4 + 2H_2O + I_2.$

Two molecules of sodium iodide and 1 molecule of manganese dioxide and 2 molecules of sulphuric acid yield 1 molecule of sodium sulphate, 1 molecule of manganese sulphate, 2 molecules of water, and 1 molecule of iodine. See Art. **79.**

(69) See Art. **134.**

(70) (*a*) A unit of heat is the amount of heat required to raise 1 gram of water from 0° to 1°.

(*b*) 34,462 units of heat. See Art. **5.**

(71) See Art. **99.**

(72) A reducing agent is a substance that removes oxygen, or elements similar to it, from its compounds, or decreases the valence of a substance, changing it from a higher to a lower state of oxidation.

(73) (*a*) See Art. **122.**

(*b*) $SO_2$.

(74) (*a*) and (*b*) See Art. **16.**

(75) The antiseptic or antizymotic property of a substance is that property which prevents or destroys putrefaction.

(76) (*a*) See Art. **54,** and Fig. 28.

(*b*) $NaCl + H_2SO_4 = HCl + NaHSO_4$

or with the application of heat,

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$

(77) (*a*) See Art. **123.**

(*b*) See Art. **129.**

(78) See Art. **47.**

(79) See Art. **11.**

(80) A suitable freezing mixture is prepared by mixing 2 parts of ice with 1 part of ordinary salt.

(81) See Art. **105.**

(82) See Art. **14,** Experiment 17.

(83) (*a*) See Art. **77.**

(*b*) See Arts. **76** and **77.**

(84) See Art. **126.**

(85) See Art. **128.**

(86) See Art. **109.**

(87) See ozone, Arts. **13** and **16.**

(88) See Art. **127.**

(89) $SO_2$ is obtained according to the equation

$$\underset{64}{S_2} + \underset{64}{2O_2} = \underset{128}{2SO_2}$$

Using formula **10,** *Theoretical Chemistry,*

$$w = \frac{Wm}{M},$$

and substituting the known values, we obtain

$$w = \frac{10 \times 128}{64} = 20 \text{ grams of } SO_2. \quad \text{Ans.}$$

# INORGANIC CHEMISTRY.

(PART 2.)

(1) $3CaF_2 + B_2O_3 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 2BF_3$

| calcium fluoride | boric oxide | sulphuric acid | calcium sulphate | water | boron fluoride |
|---|---|---|---|---|---|

(2) (*a*) For the preparation of carbon dioxide see Art. **119.**

(*b*) $$\underset{100}{CaCO_3} = \underset{56}{CaO} + \underset{44}{CO_2}$$

Using formula **6,** Art. **84,** *Theoretical Chemistry,*

$$z = \frac{m \times y}{a\,n},$$

we obtain $z = \dfrac{100 \times 594}{44} = 1{,}350$ grams of calcium carbonate. Ans.

Or, $$\underset{100}{CaCO_3} + \underset{73}{2HCl} = \underset{111}{CaCl_2} + \underset{18}{H_2O} + \underset{44}{CO_2}$$

$$z = \frac{100 \times 594}{44} = 1{,}350 \text{ grams of calcium carbonate. Ans.}$$

(3) See Table 1, Art. **7.**

(4) (*a*) Using formula **2,** Art. **82,** *Theoretical Chemistry,*

$$n = \frac{m\,x}{100\,a},$$

and substituting the known values, we obtain

$$n = \frac{108 \times 25.93}{100 \times 14} = 2N, \qquad n = \frac{108 \times 74.07}{100 \times 16} = 5O.$$

Its formula, therefore, is $N_2O_5$. Ans.

(*b*) Nitric oxide, etc. See Art. **32.**

(5) Calcium carbonate has the formula

$$\underbrace{\underset{40+12+48}{CaCO_3}}_{100 \text{ molecular weight},}$$

which shows that calcium carbonate contains 40% of calcium; hence, 1,000 kilograms of $CaCO_3$ must contain 400 kilograms of calcium. Ans.

(6) See Art. **148.**

(7) Ammonia has the formula $NH_3$, and a molecular weight of 17. Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

we obtain $$x = \frac{100 \times 14 \times 1}{17} = 82.353\%\ N,$$

$$x = \frac{100 \times 1 \times 3}{17} = 17.647\%\ H. \quad \text{Ans.}$$

(8) See Art. **3.**

(9) Cyanogen; the specific gravity and characteristic odor are mentioned in Art. **155,** and the density is given (in Italics) below the heading "Cyanogen."

(10) See Art. **134.**

(11) $CuHAsO_3$.

(12) See Art. **46.**

(13) One liter of nitrogen, i. e., 1,000 c. c., weighs 1.255 grams; 250 c. c. must, therefore, weigh .31375 gram. Ans.

(14) (*a*) See Art. **105.**

(*b*) See Art. **106.**

(15) $SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl.$

(16) See Art. **8.**

(17) $(OH)H_2N.$

(18) $H_2NaPO_4$, dihydrosodium phosphate.
$HCaPO_4$, hydrocalcium phosphate.
$BiPO_4$, bismuth phosphate.

(19) (*a*) Arsenate of soda, $Na_2HAsO_4, 7Aq$.

(*b*) Calcium arsenate, $CaHAsO_4, 7Aq$.

(20) See Art. **114.**

(21) See Art. **141.**

(22) Carbon disulphide is formed according to the equation:

$$\underset{24}{C_2} + \underset{128}{2S_2} = \underset{152}{2CS_2}$$

Using formula **8,** Art. **85,** *Theoretical Chemistry,*

$$W = \frac{Mw}{m},$$

and substituting the proper values, we obtain

$$W = \frac{64 \times 76}{76} = 64 \text{ grams of } S. \quad \text{Ans.}$$

(23) Borax has the formula $Na_2B_4O_7$; its molecular weight, consequently, is 202. Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

we obtain

$$x = \frac{100 \times 23 \times 2}{202} = 22.77\%\ Na,$$

$$x = \frac{100 \times 11 \times 4}{202} = 21.78\%\ B,$$

$$x = \frac{100 \times 16 \times 7}{202} = 55.45\%\ O. \quad \text{Ans.}$$

(24) $H_3PO_4$ is phosphoric acid. See Art. **59** for its properties. $PH_3$ is phosphine. See Art. **54** for its properties.

(25) Nitrogen dioxide is obtained according to the equation:

$$\underset{189}{3Cu} + \underset{504}{8HNO_3} = \underset{561}{3Cu(NO_3)_2} + \underset{60}{N_2O_2} + \underset{72}{4H_2O}$$

and, as 1 liter of nitrogen dioxide weighs 1.33 grams, 100 liters weigh 133 grams.

As 60 : 189 :: 133 : 418.95

so is 60 : 504 :: 133 : 1,117.2

from which it follows that, in order to produce 100 liters of nitrogen dioxide, 418.95 grams of copper and 1,117.2 grams of nitric acid are required. Ans.

(26) See Art. **38.**

(27) (*a*) and (*b*) See Art. **74.**

(28) See Art. **90.**

(29) See Art. **121.**

(30) (*a*) See Art. **102.**
(*b*) See Art. **103.**

(31) See Art. **138.**

(32) See Art. **154,** Experiment 41.

(33) Carbon dioxide is formed according to the equation:

$$\underset{12}{C} + \underset{32}{O_2} = \underset{44}{CO_2}$$

Using formula **5,** Art. **84,** *Theoretical Chemistry,*

$$y = \frac{a\,n \times z}{m},$$

and substituting the proper values, we obtain

$$y = \frac{44 \times 48}{12} = 176 \text{ grams of } CO_2. \quad \text{Ans.}$$

(34) See Art. **14.**

(35) See Art. **15.**

(36) Nitrogen, with which oxygen is mixed in air, is a very inert gas, and does not support combustion.

(37) See Art. **78.**

(38) From the question, there are 23 grams of $O$ in 100 grams of air. The chemical action when $P$ burns in $O$ is represented in the following equation:

$$\underset{62}{2P} + \underset{80}{5O} = \underset{142}{P_2O_5}$$

To burn 80 by weight of $O$, 62 of $P$ are required; then, the number of grams of $P$ required to burn 23 grams of $O$ is determined by the proportion

80 : 23 :: 62 : 17.8. Ans.

(39) $CO_2 + H_2O = H_2CO_3.$

(40) $CuO + CO = Cu + CO_2.$

(41) $\underset{12}{C} + \underset{32}{O_2} = \underset{44}{CO_2}.$

As 12 parts of $C$ require 32 parts of $O$, 1,000 kilograms will require 2,666.6 kilograms of $O$; and, as 1 liter of oxygen, i. e., 1 cubic decimeter, weighs 1.429 grams, 1,000 cubic decimeters, or 1 cubic meter, weigh 1,429 grams, or

1.429 kilograms of $O$ = 1 cubic meter;

hence, 2,666.6 kilograms of $O$ = 1,866.06 cubic meters. Ans.

(42) Ammonia is formed according to the equation:

$$\underset{107}{2NH_4Cl} + \underset{56}{CaO} = \underset{111}{CaCl_2} + \underset{18}{H_2O} + \underset{34}{2NH_3}$$

Employing formula **8**, Art. **85**, *Theoretical Chemistry*,

$$W = \frac{Mw}{m},$$

and substituting the proper values (necessarily taking 34 for $m$), we obtain

$$W = \frac{56 \times 59}{34} = 97.17 \text{ grams of } CaO. \quad \text{Ans.}$$

(43) The formula of ethylene gas is $H_4C_2$; its molecular weight is 28. Using formula **1**, Art. **81**, *Theoretical Chemistry*,

$$x = \frac{100\,a\,n}{m},$$

we obtain

$$H = \frac{100 \times 1 \times 4}{28} = 14.28\% \text{ of } H,$$

$$C = \frac{100 \times 12 \times 2}{28} = 85.72\% \text{ of } C.$$

(44) See Art. **122**, *Theoretical Chemistry*, and Art. **142**, of this paper.

(45) See Art. **157**.

(46) $Si + 3HCl = SiHCl_3 + H_2.$

(47) Referring to Art. **14**, it will be seen that (*a*) at 0° one volume of water absorbs 1,149 volumes of ammonia gas;

consequently, 3.92 liters will absorb 4,504.08 liters; (*b*) at 15° one volume of water absorbs 783 volumes of ammonia gas, or 3.92 liters will absorb 3,069.36 liters.

(48) $N_2O$, or hyponitrous oxide, is prepared according to the following equation (see Art. **24**):

$$\underset{630}{10HNO_3} + \underset{260}{4Zn} = \underset{44}{N_2O} + \underset{756}{4Zn(NO_3)_2} + \underset{90}{5H_2O}$$

Using formula **10,** Art. **85,** *Theoretical Chemistry,*

$$w = \frac{Wm}{M},$$

and substituting the proper values, we obtain

$$w = \frac{.44 \times 1}{260} = .169 \text{ kilogram of } N_2O;$$

and, as 1.97 grams of hyponitrous oxide occupy the volume of 1 liter, .169 kilo, or 169 grams, occupy the volume of 85.787 liters. Ans.

(49) See Art. **40.**

(50) See Arts. **47** and **48.**

(51) The best antidotes, in case of poisoning from arsenic, are freshly prepared ferric or magnesic hydrate, which form insoluble compounds with the arsenic and thus render this poison comparatively harmless.

(52) See Art. **94.**

(53) Carbon monoxide is obtained from oxalic acid according to the equation:

$$\underset{90}{H_2C_2O_4} = \underset{18}{H_2O} + \underset{44}{CO_2} + \underset{28}{CO}$$

Using formula **10,** Art. **85,** *Theoretical Chemistry,*

$$w = \frac{Wm}{M},$$

and substituting the known values, we obtain

$$\frac{100 \times 28}{90} = 31.11 \text{ grams of } CO.$$

1.25 grams of $CO$ occupy the volume of 1 liter; and, consequently, 31.11 grams occupy the volume of 24.88 liters. Ans.

(54) See Art. **156.**

(55) Nitric acid is obtained by the action of sulphuric acid on sodium nitrate, according to the equation:

$$\underset{85}{NaNO_3} + \underset{98}{H_2SO_4} = \underset{63}{HNO_3} + \underset{120}{NaHSO_4}$$

Using formula **10,** Art. **85,** *Theoretical Chemistry,*

$$w = \frac{Wm}{M},$$

and substituting the known values, we obtain

$$w = \frac{63 \times 170}{85} = 126 \text{ grams of nitric acid.} \quad \text{Ans.}$$

(56) As 100 c. c. of ammonia give 200 c. c. of a mixture of hydrogen and nitrogen, i. e., 150 c. c. of $H$ and 50 c. c. of $N$ (see Art. **17**), 250 c. c. of ammonia, on being decomposed by electric sparks, will give 500 c. c. of mixed gases.

(57) Phosphorus pentoxide is obtained synthetically by burning phosphorus in oxygen, according to the equation:

$$\underset{124}{P_4} + \underset{160}{5O_2} = \underset{284}{2P_2O_5}$$

Using formula **5** or formula **10,** Arts. **84** and **85,** *Theoretical Chemistry,*

$$y = \frac{an \times z}{m},$$

and substituting the known values, we obtain

$$y = \frac{284 \times 793}{124} = 1{,}816.22 \text{ grams of phosphorus pentoxide.}$$

Ans.

(58) (*a*) See Art. **39.**

(*b*) Two hundred and fifty c. c. of nitric acid and 750 c. c. of hydrochloric acid.

(59) See Arts. **58** and **59.**

(60) See Art. **100.**

(61) Carbonic acid is a dibasic acid, because it contains two replaceable atoms of $H$.

(62) See Art. **144.**

(63) See Art. **165.**

(64) The equations are

$$\underset{73}{2HCl} + \underset{65}{Zn} = \underset{136}{ZnCl_2} + \underset{2}{H_2}$$

$$\underset{73}{2HCl} + \underset{100}{CaCO_3} = \underset{111}{CaCl_2} + \underset{18}{H_2O} + \underset{44}{CO_2}$$

An inspection of the equation shows that 2 molecules of the hydrochloric acid cause, respectively, the evolution of 1 molecule of hydrogen $H_2$ and 1 molecule of carbon dioxide; and the volume of gases must, according to Avogadro's law, be the same, and must be one-half the volume of the hydrochloric acid used.

As 1 liter of hydrochloric acid weighs 1.63 grams, 10 grams occupy 6.135 liters, and the hydrogen and carbon dioxide evolved each occupy 3.0675 liters. Ans.

(65) See Art. **41.**

(66) See Art. **71.**

(67) See Art. **109.**

(68) See Art. **120.**

(69) Cyanogen is prepared from cyanide of mercury, according to the equation:

$$\underset{252}{Hg(CN)_2} = \underset{200}{Hg} + \underset{52}{(CN)_2}$$

Using formula **6,** Art. **84,** *Theoretical Chemistry,*

$$z = \frac{m \times y}{a\,n},$$

and substituting the known values, we obtain

$$z = \frac{252 \times 50}{52} = 242.308 \text{ grams. Ans.}$$

(70) $N_2O$, 28 parts of $N$ and 16 parts of $O$.
$N_2O_2$, 28 parts of $N$ and 32 parts of $O$.
$N_2O_3$, 28 parts of $N$ and 48 parts of $O$.
$N_2O_4$, 28 parts of $N$ and 64 parts of $O$.
$N_2O_5$, 28 parts of $N$ and 80 parts of $O$.

(71) (*a*) The formula of phosphine is $H_3P$.

(*b*) See Art. **53.**

(*c*) The reaction—a somewhat complicated one—may be expressed thus:

$$P_4 + 3KOH + 3H_2O = 3KH_2PO_2 + H_3P$$

(72) No; the reason for this is given in that part of Art **43** which refers to Experiment 5.

(73) Whether this white powder is arsenious oxide, or at least contains some, may be ascertained by sprinkling it upon a red-hot coal. If a garlic-like odor is perceptible, this may be taken as an indication that the powder in question contains arsenious oxide.

(74) From the given equation:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

we find that 1 volume of marsh gas requires 2 volumes of oxygen; therefore, 100 measures will require 200 measures of pure oxygen. Air contains 21%, by volume, of oxygen; therefore,

$$21 : 200 :: 100 : 952 \text{ volumes of pure air.}$$

(75) (*a*) See Art. **111.**

(*b*) See Art. **112.**

(76) Carbon disulphide is obtained according to the following equation:

$$\underset{24}{C_2} + \underset{128}{2S_2} = \underset{152}{2CS_2}$$

1 liter of carbon-disulphide vapor weighs 3.40 grams; the desired 1.25 liters, consequently, weigh 4.25 grams. Using formula **8,** Art. **85,** *Theoretical Chemistry,*

$$W = \frac{Mw}{m},^*$$

and substituting the proper values, we obtain

$$W = \frac{128 \times 4.25}{152} = 3.578 \text{ grams of } S. \quad \text{Ans.}$$

*In stating these formulas in *Theoretical Chemistry*, it has, of course, been assumed that each molecule of the factor yielded one of the products. If in any reaction this is not true, then $M$ and $m$ must represent the sum of the molecular weights expressed in the equation.

(77) Hyponitrous oxide, also known as "laughing gas," is widely used in surgery and dentistry (see Art. **25**).

(78) See Art. **70.**

(79) Methane is obtained from sodium acetate (see Art. **103**) according to the equation:

$$\underset{82}{NaC_2H_3O_2} + \underset{40}{NaOH} = \underset{106}{Na_2CO_3} + \underset{16}{H_4C}$$

Employing formula **10,** Art. **85,** *Theoretical Chemistry,*

$$w = \frac{Wm}{M},$$

and substituting the proper values, we obtain

$$w = \frac{888 \times 16}{82} = 173.26 \text{ grams of methane;}$$

and, as 1 liter of methane weighs .715 gram, 173.26 grams would occupy the volume of 242.32 liters. Ans.

(80) Carbon monoxide does not render lime water milky.

(81) $KH_2PO_4$.

(82) (*a*) and (*b*) See Art. **162.**

(83) $N_2O$ is obtained from ammonium nitrate according to the equation:

$$\underset{80}{(NH_4)NO_3} = \underset{44}{N_2O} + \underset{36}{2H_2O}$$

Employing formula **5,** Art. **84,** *Theoretical Chemistry,*

$$y = \frac{an \times z}{m},$$

and substituting the proper values, we obtain

$$y = \frac{44 \times 15}{80} = 8.25 \text{ grams;}$$

and, as 1.97 grams of $N_2O$ occupy the volume of 1 liter, 8.25 grams will occupy the volume of 4.188 liters. Ans.

(84) See Art. **152.**

(85) (*a*) and (*b*) See Art. **127.**

(*c*) See Arts. **127, 128, 129,** and **130.**

(86) See Art. **120.**

(87) See Art. **79.**

(88) Either by subjecting it to a pressure of 6½ atmospheres at 10° or by cooling it to −40°.

(89) See Art. **45.**

(90) Arsenic disulphide, or realgar, $As_2S_2$.
Arsenic trisulphide, or orpiment, $As_2S_3$.
Arsenic pentasulphide, $As_2S_5$.

(91) (*a*) See Art. **160.**
(*b*) $SiO_2$.

(92) Arsenious oxide, $As_2O_3$.
Arsenic oxide, $As_2O_5$.

(93) See Art. **58** and Experiment **13.**

(94) See Art. **7.**

# INORGANIC CHEMISTRY.

**(PART 8.)**

(1) $Sc_2O_3$.

(2) (1) $$\underset{142}{Na_2SO_4} + \underset{24}{C_2} = \underset{78}{Na_2S} + \underset{88}{2CO_2}$$

(2) $$\underset{78}{Na_2S} + \underset{100}{CaCO_3} = \underset{106}{Na_2CO_3} + \underset{72}{CaS}$$

Using formula **10**, Art. **85**, *Theoretical Chemistry*, we obtain

for (*a*) $$w = \frac{71 \times 78}{142} = 39;$$

$$w = \frac{39 \times 106}{78} = 53 \text{ Kg.} \quad \text{Ans.}$$

For (*b*) $$w = \frac{426 \times 78}{142} = 234;$$

$$w = \frac{234 \times 106}{78} = 318 \text{ Kg.} \quad \text{Ans.}$$

(3) See Art. **28.**

(4) See Art. **2.**

(5) See Art. **151.**

(6) $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. One molecule of calcium carbide plus 2 molecules of water = 1 molecule of calcium hydrate plus 1 molecule of acetylene.

(7) $Ca(OH)_2$.

(8) A saturated solution of sodium chloride boils at 109.7°. See Art. **70.**

(9) See Art. **13.**

(10)
$$\underbrace{\underset{69}{Na_3}\ \underset{27.5}{Al}\ \underset{114}{F_6}}_{210.5}$$

Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

and substituting the proper values, we obtain

$$x = \frac{100 \times 27.5 \times 1}{210.5} = 13.064\%\ Al. \quad \text{Ans.}$$

(11) See Art. **20.**

(12) The spectrum of lithium is characterized by an intense crimson line, having a wave length of .0006705 mm.

(13) See Art. **34.**

(14) Acetylene is obtained according to the formula:

$$\underbrace{\underset{40+24}{CaC_2} + \underset{(2+16)2}{2H_2O}}_{64\ +\ 36} = \underbrace{\underset{40+34}{Ca(OH)_2} + \underset{24+2}{C_2H_2}}_{74\ +\ 26}$$

We further know that 1 liter of $C_2H_2$ weighs 1.16 grams; hence, 29 liters weigh 33.64 grams.

Employing, now, formula **8,** Art. **85,** *Theoretical Chemistry,*

$$W = \frac{M w}{m},$$

we obtain $$W = \frac{64 \times 33.64}{26} = 82.806 \text{ g.} \quad \text{Ans.}$$

(15) Artificial barium sulphate. See Art. **112.**

(16) See Arts. **14, 15,** and **16.**

(17) See Art. **46.**

(18) Metallic carbonates, with the exception of the alkaline carbonates, are insoluble in pure water. See Art. **38.**

(19) See Art. **2.**

(20) Sodium carbonate has the formula $Na_2CO_3$ and a molecular weight of 106.

Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

we obtain

$$\text{sodium} = \frac{100 \times 23 \times 2}{106} = 43.396\%;$$

$$\text{carbon} = \frac{100 \times 12 \times 1}{106} = 11.321\%;$$

$$\text{oxygen} = \frac{100 \times 16 \times 3}{106} = 45.283\%. \quad \text{Ans.}$$

(21) $NH_4HCO_3$.

(22) Valence II.

(23) See Art. **42.**

(24) $3Cl_2 + 6KOH = KClO_3 + 5KCl + 3H_2O$.

(25) See Art. **170.**

(26) See Art. **2.**

(27) Symbol *In*. Atomic weight 113.4. Valence II and III.

(28) Barium occurs in nature as barium carbonate in the mineral *witherite*, and as barium sulphate in *heavy spar*, or *barites*. See Art. **104.**

(29) See Art. **26.**

(30) Magnesia, or magnesium oxide, has the formula $MgO$.

(31) $$\underset{100}{CaCO_3} = \underset{44}{CO_2} + \underset{56}{CaO}$$

Using formula **10,** Art. **85,** *Theoretical Chemistry,*

$$w = \frac{Wm}{M}$$

$$w = \frac{139 \times 56}{100} = 77.84 \text{ Kg.} \quad \text{Ans.}$$

(32) See Art. **84.**

(33) See Art. **13.**

(34) $G_2O_3$.

(35) Symbol $Li$. Atomic weight 7.01. For its properties see Art. **98.**

(36) (*a*) and (*b*) See Art. **39.**

(37) $K_2CO_3 + H_2C_4H_4O_6 = KHC_4H_4O_6 + KHCO_3$.

(38) (*a*) and (*b*) See Art. **17.**

(39) (*a*) Zinc blende has the formula $ZnS$, and a molecular weight of 97. Employing formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

we obtain $$x = \frac{100 \times 65 \times 1}{97} = 67\%. \quad \text{Ans.}$$

(*b*) Smithsonite has the formula $ZnCO_3$ and a molecular weight of 125. Employing the same formula, we obtain

$$x = \frac{100 \times 65 \times 1}{125} = 52\%. \quad \text{Ans.}$$

(40) $AlCl_3$ or $Al_2Cl_6$.

(41) See Art. **8.**

(42) The name cæsium has been derived from the Latin *cæsius* (sky blue), and has reference to the two bright blue lines which distinguish the spectrum of this metal.

(43) See Art. **151.**

(44) Yes; see Art. **32.**

(45) Strontianite has the formula $SrCO_3$, and, therefore, contains 32.61 per cent. of oxygen. Witherite has the formula $BaCO_3$, and contains 24.39 per cent. of oxygen. Strontianite, therefore, contains 8.22 per cent. more oxygen than witherite.

(46) (*a*) 900 parts of gold,
100 parts of copper.

(*b*) 90 to 95 parts of copper,
10 to 5 parts of aluminum.

(*c*) 100 parts of tin,
8 parts of antimony,
1 part of bismuth,
4 parts of copper.

(47) See Art. **26.**

(48) See Art. **68.**

(49)
$$\underset{138}{K_2CO_3} + \underset{74}{Ca(OH)_2} = \underset{100}{CaCO_3} + \underset{112}{2KOH}$$

If 138 Kg. of $K_2CO_3$ yield 112 Kg. of $KOH$, 69 Kg. of $K_2CO_3$ will yield 56 Kg. of $KOH$. Ans.

(50) See Art. **149.**

(51) Calcium hydrate is obtained according to the equation:

$$\underset{56}{CaO} + \underset{18}{H_2O} = \underset{74}{Ca(OH)_2}$$

Using formula **10,** Art. **85,** *Theoretical Chemistry,*

$$w = \frac{Wm}{M},$$

and substituting the proper values, we obtain

$$w = \frac{250 \times 74}{56} = 330.357 \text{ Kg. Ans.}$$

(52) Rubidium was discovered by *Bunsen* in 1860 in the waters of the Durckheim Springs.

(53) See Art. **11.**

(54) Aluminum oxide occurs in nature as the minerals corundum, ruby, and sapphire. See Art. **169.**

(55) (*a*) and (*b*) See Art. **43.**

(56) $NH_4NO_3$.

(57) $5MgCO_3, 2Mg(OH)_2, 7Aq$.

(58) All metallic sulphates are soluble in water, except those of barium, strontium, and lead, which are almost entirely insoluble, and those of silver and calcium, as well as mercurous sulphate, which are only slightly soluble in water. See Art. **35.**

(59) (*a*) and (*b*) See Art. **106.**

(60) Common salt has the formula $NaCl$, and its molecular weight is 58.5. Using formula **1,** Art. **81,** *Theoretical Chemistry*, we obtain

$$\text{sodium} = \frac{100 \times 23 \times 1}{58.5} = 39.32\%;$$

$$\text{chlorine} = \frac{100 \times 35.5 \times 1}{58.5} = 60.68\%. \quad \text{Ans.}$$

(61) See Art. **22.**

(62) See Arts. **32** and **33.**

(63) See Art. **43.**

(64) $MgSO_4, H_2O, 6Aq$.

(65) See Art. **127.**

(66) The formula of borax is $Na_2B_4O_7$, and its molecular weight is 202. Using formula **1,** Art. **81,** *Theoretical Chemistry*,

$$x = \frac{100\,a\,n}{m},$$

we obtain

$$\text{sodium} = \frac{100 \times 23 \times 2}{202} = 22.772\%;$$

$$\text{boron} = \frac{100 \times 11 \times 4}{202} = 21.782\%;$$

$$\text{oxygen} = \frac{100 \times 16 \times 7}{202} = 55.446\%. \quad \text{Ans.}$$

(67) Silicic oxide has the formula $SiO_2$ and a molecular weight of 60. Aluminum oxide has the formula $Al_2O_3$, and a molecular weight of 103. Employing formula **2**, Art. **82**, *Theoretical Chemistry*,

$$n = \frac{m\,x}{100\,a},$$

we obtain $$n = \frac{163 \times 36.8}{100 \times 60} = 1,$$

and $$n = \frac{163 \times 63.2}{100 \times 103} = 1;$$

or, in other words, the mineral fibrolite contains 1 molecule of silicic oxide and 1 molecule of aluminum oxide, hence its formula is $SiO_2, Al_2O_3$. Ans.

(68) See Art. **12.**

(69) See Art. **27.**

(70) Symbol *Ca*. Atomic weight 39.9. Valence II.

(71) Using formula **2**, Art. **82**, *Theoretical Chemistry*,

$$n = \frac{m\,x}{100\,a},$$

and substituting the proper values, we obtain

$$\text{magnesium} = \frac{246 \times 9.76}{24 \times 100} = 1;$$

$$\text{sulphur} = \frac{246 \times 13.01}{32 \times 100} = 1;$$

$$\text{oxygen} = \frac{246 \times 26.01}{16 \times 100} = 4;$$

$$\text{water} = \frac{246 \times 51.22}{18 \times 100} = 7.$$

Hence, the formula of this salt must be $MgSO_4, 7H_2O$, and its name is Epsom salt.

(72) See Art. **55.**

(73) Potassium. See Art. **18.**

(74) See Art. **36.**

(75) See Art. **42.**

(76) Cæsium was discovered simultaneously with rubidium by *Bunsen* in 1860 (see Art. **100**), and was obtained in the pure state by *Setterberg* in 1882. See Art. **102.**

(77) See Art. **169.**

(78) See Arts. **23** and **24.**

(79) $BaO_2$.

(80) Potassium chlorate is formed (see Art. **57**) according to the equation:

$$\underset{213}{3Cl_2} + \underset{336}{6KOH} = \underset{122.5}{KClO_3} + \underset{372.5}{5KCl} + \underset{54}{3H_2O}$$

Using formula **8**, Art. **85**, *Theoretical Chemistry*, and substituting the proper values, we obtain

$$(a) \quad W = \frac{35.5 \times 6 \times 336}{122.5} = 584.23 \text{ Kg.} \quad \text{Ans.}$$

$$(b) \quad W = \frac{35.5 \times 6 \times 200}{122.5} = 347.76 \text{ g.} \quad \text{Ans.}$$

(81) See Art. **100.**

(82) See Art. **131.**

(83) See Art. **87.**

(84) The alkaline sulphides, and those of calcium, barium, and strontium, are soluble in water.

(85) See Arts. **159–164.**

(86) See Art. **19.**

(87) See Art. **45.**

(88) Barium chlorate has the formula $Ba(ClO_3)_2$, and a molecular weight of 304. Using formula **1**, Art. **81**, *Theoretical Chemistry*,

$$x = \frac{100\,a\,n}{m},$$

and substituting the proper values, we obtain

$$\text{barium, } x = \frac{137 \times 100}{304} = 45.07\%;$$

$$\text{chlorine, } x = \frac{35.5 \times 2 \times 100}{304} = 23.35\%;$$

$$\text{oxygen, } x = \frac{16 \times 6 \times 100}{304} = 31.58\%. \text{ Ans.}$$

(89) (*a*) and (*b*) See Art. **48.**

# INORGANIC CHEMISTRY.

(PART 4.)

(1) $HNbO_3$.

(2) See Art. **214.**

(3) See Art. **2.**

(4) Niccolite has the formula $NiAs$; its molecular weight, therefore, is 133.5. Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

we find nickel $= x = \frac{100 \times 58.6 \times 1}{133.5} = 43.90\%$. Ans.

(5) Stannous chloride has the formula $SnCl_2$ and a molecular weight of 189. Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

we find that stannous chloride contains 37.56% of chlorine, or .3756 gram of chlorine in 1 gram of stannous chloride. 3.17 grams of chlorine occupy 1 liter; hence, .3756 gram of chlorine occupies the volume of .1185 liter, or 118.5 cubic centimeters.

(6) See Art. **160.**

(7) See Art. **191.**

(8) Cobaltous nitrate is formed according to the equation:

$$\underset{74.5}{CoO} + \underset{126}{2HNO_3} = \underset{182.5}{Co(NO_3)_2} + \underset{18}{H_2O}$$

Using formula **6**, Art. **84**, *Theoretical Chemistry*,

$$z = \frac{m \times y}{a\,n},$$

and substituting the proper values, we obtain

$$z = \frac{74.5 \times 36}{182.5} = 14.69 \text{ g.} \quad \text{Ans.}$$

(9) Chrome alum is formed according to the equation:

$$\underset{295}{K_2Cr_2O_7} + \underset{98}{H_2SO_4} + \underset{192}{3SO_2} = \underset{567}{2KCr(SO_4)_2} + \underset{18}{H_2O}$$

(*a*) Using formula **6**, Art. **84**, *Theoretical Chemistry*, and substituting the proper values, we obtain

$$K_2Cr_2O_7 = z = \frac{295 \times 998}{567} = 519.24 \text{ g.} \quad \text{Ans.}$$

$$H_2SO_4 = z = \frac{98 \times 998}{567} = 172.5 \text{ g.} \quad \text{Ans.}$$

(*b*) The solution of this question may be easily derived by simple proportion; that is,

$$567 : 18 = 998 : x = 31.682 \text{ g. } H_2O. \quad \text{Ans.}$$

(10) See Art. **177**.

(11) $Fe_2O_3$.

(12) Silver nitrate has the formula $AgNO_3$ and a molecular weight of 170. Using formula **1**, Art. **81**, *Theoretical Chemistry*,

$$x = \frac{100\,a\,n}{m},$$

and substituting the proper values, we obtain

$$x = \frac{100 \times 108 \times 1}{170} = 63.53\% \text{ silver.} \quad \text{Ans.}$$

(13) $Co_3O_4$ or $CoO, Co_2O_3$.

(14) See Art. **206.**

(15) See Art. **32.**

(16) $GeCl_4$.

(17) (*a*) $K_2CrO_4$.
(*b*) $PbCrO_4$.
(*c*) $K_2CrO_4, CrO_3$ or $K_2Cr_2O_7$.

(18) See Art. **168.**

(19) See Art. **16.**

(20) See Arts. **86** and **87.**

(21) See Art. **146.**

(22) $$\underset{295}{K_2Cr_2O_7} + \underset{24}{C_2} = \underset{153}{Cr_2O_3} + \underset{138}{K_2CO_3} + \underset{28}{CO}$$

Using formula **5,** Art. **84,** *Theoretical Chemistry,*

$$y = \frac{a\,n \times z}{m},$$

and substituting the proper values, we obtain

$$y = \frac{153 \times 853}{295} = 442.4 \text{ g.} \quad \text{Ans.}$$

(23) Red hematite has the formula $Fe_2O_3$.
Iron pyrites has the formula $FeS_2$.
Magnetic iron ore has the formula $Fe_3O_4$.

Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

and substituting the proper values, we obtain

(*a*) $\text{red hematite} = x = \frac{100 \times 56 \times 2}{160} = 70\%$. Ans.

(*b*) $\text{iron pyrites} = x = \frac{100 \times 56 \times 1}{120} = 46.66\%$. Ans.

(*c*) $\text{magnetic iron ore} = x = \frac{100 \times 56 \times 3}{232} = 72.41\%$. Ans.

(24) Malachite has the formula $CuCO_3, Cu(OH)_2$ and a molecular weight of 220; hence, by proportion,

$$220 : 126 = 1{,}000 : x,$$

we obtain the weight of copper contained in 1,000 kilograms of malachite, i. e., 572.73 Kg.

(25) $PtCl_4$ has a molecular weight of 339. The formula then shows, that in 339 grams of $PtCl_4$, there are 142 grams of chlorine combined with 197 grams of $Pt$; and in 1 gram of $PtCl_4$, there is .419 gram of chlorine gas. According to *Inorganic Chemistry*, Part 1, 3.17 grams of chlorine gas occupy the volume of 1 liter, or 1,000 cubic centimeters, and, consequently, .419 gram of chlorine will occupy 132.176 cubic centimeters.

(26) See Art. **114.**

(27) See Art. **59.**

(28) Stannic chloride may be prepared by the direct union of chlorine and tin (see Art. **118**). The union may be expressed by the equation:

$$\underset{118}{Sn} + \underset{142}{Cl_4} = \underset{260}{SnCl_4}$$

which shows that 142 grams of chlorine are required to change 118 grams of tin into stannic chloride.

Chlorine gas is prepared according to the equation (see Art. **45,** *Inorganic Chemistry*, Part 1):

$$\underset{146}{4HCl} + \underset{87}{MnO_2} = \underset{126}{MnCl_2} + \underset{36}{2H_2O} + \underset{71}{Cl_2}$$

Using formula **6,** Art. **84,** *Theoretical Chemistry*,

$$z = \frac{m \times y}{a\,n},$$

and substituting the proper values, we obtain

$$HCl = z = \frac{146 \times 142}{71} = 292 \text{ g. Ans.}$$

$$MnO_2 = z = \frac{87 \times 142}{71} = 174 \text{ g. Ans.}$$

(29) *Bi*, *Sb*, *Ta*, *Nb*, and *V*. See also Art. **113.**

(30) $CuSO_4, 5H_2O$.

(31) Let $x$ represent the percentage of *Au*.
Let $y$ represent the percentage of *Pt*.

The Sp. Gr. of gold is 19.33, and of platinum is 21.5.

$$x+y = 100\%. \qquad (1)$$

$$19.33x+21.5y = 20\times 100 = 2{,}000. \qquad (2)$$

Multiplying (1) by 19.33, and subtracting from (2), we have

$$\begin{array}{rcl} 19.33x+21.5y & = & 2{,}000 \\ \underline{19.33x+19.33y} & \underline{=} & \underline{1{,}933} \\ 2.17y & = & 67 \\ y & = & 30.87\%.\ Pt. \quad \text{Ans.} \end{array}$$

(32) $NH_4VO_3$.

(33) $Co_3(AsO_4)_2, 8Aq$.

(34) See Art. **134.**

(35) See Art. **75.**

(36) See Art. **19.**

(37) $HgCl_2$ is formed according to the equation:

$$\underset{296}{HgSO_4} + \underset{117}{2NaCl} = \underset{142}{Na_2SO_4} + \underset{271}{HgCl_2}$$

Using formula **6,** Art. **84,** *Theoretical Chemistry,*

$$z = \frac{m\times y}{a\,n},$$

and substituting the proper values, we obtain

$$HgSO_4 = z = \frac{296\times 500}{271} = 546.1 \text{ g.} \quad \text{Ans.}$$

$$NaCl = z = \frac{117\times 500}{271} = 215.9 \text{ g.} \quad \text{Ans.}$$

(38) See Art. **30.**

(39) Uranium belongs to the chromium family of metals (see Art. **91**).

(40) See Art. **124.**

(41) Manganous sulphide has the formula *MnS*; its molecular weight is 87. Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

and substituting the proper values, we obtain

$$Mn = x = \frac{100 \times 55 \times 1}{87} = 63.22\%. \quad \text{Ans.}$$

$$S = x = \frac{100 \times 32 \times 1}{87} = 36.78\%. \quad \text{Ans.}$$

(42) See Art. **2.**

(43) $MoS_2$.

(44) $Ta_2O_4$ and $Ta_2O_5$.

(45) (*a*) $Hg_2SO_4$.
(*b*) $HgSO_4$.

(46) Stannic chloride is prepared according to the equation:

$$\underset{118}{Sn} + \underset{542}{2HgCl_2} = \underset{260}{SnCl_4} + \underset{400}{2Hg}$$

Using formula **6,** Art. **84,** *Theoretical Chemistry,*

$$z = \frac{m \times y}{a\,n},$$

and substituting the proper values, we obtain

$$z = \frac{118 \times 962}{260} = 436.6 \text{ g. tin.} \quad \text{Ans.}$$

(47) See Art. **80.**

(48) (*a*) Ferric chloride ($FeCl_3$). See Art. **14.**
(*b*) Ferric chloride is formed according to the equation:

$$\underset{56}{Fe} + \underset{106.5}{3Cl} = \underset{162.5}{FeCl_3}$$

Using formula **5,** Art. **84,** *Theoretical Chemistry,*

$$y = \frac{a\,n \times z}{m},$$

and substituting the proper values, we obtain

$$y = \frac{162.5 \times 250}{56} = 725.45 \text{ g. } FeCl_3. \quad \text{Ans.}$$

(49) (*a*) Thallic hydroxide.

(*b*) Thallic sulphide.

(*c*) Thallious chloride.

(50) $MoCl_5$.

(51) $WO_3$.

(52) Antimonious sulphide has the formula $Sb_2S_3$, and a molecular weight of 336.

Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

and substituting the proper values, we obtain

$$x = \frac{100 \times 120 \times 2}{336} = 71.43\% \; Sb. \quad \text{Ans.}$$

(53) See Art. **59.**

(54) See Art. **197.**

(55)
$$\underset{477}{2PbS} + \underset{96}{3O_2} = \underset{445}{2PbO} + \underset{128}{2SO_2}$$

Using formula **5,** Art. **84,** *Theoretical Chemistry,*

$$y = \frac{a\,n \times z}{m},$$

and substituting the proper values, we obtain

$$y = \frac{128 \times 1{,}000}{477} = 268.34 \text{ Kg. } SO_2.$$

As 2.86 grams occupy the volume of 1 liter, 1 gram occupies the volume of .349 liter, and 268.34 kilograms occupy the volume of 93,650.66 liters.

(56) $Hg_2O$ has a molecular weight of 416.

Using formula **1,** Art. **81,** *Theoretical Chemistry,*

$$x = \frac{100\,a\,n}{m},$$

and substituting the proper values, we obtain

$$x = \frac{100 \times 400}{416} = 96.15\%\ Hg.$$

$$x = \frac{100 \times 16}{416} = 3.85\%\ O.$$

(57) See Art. **196.**

(58) See Art. **106.**

(59) $Na_4ZrO_4$.

(60) See Art. **198.**

(61) See Art. **198.**

(62) Silver nitrate may be formed according to the equation:

$$\underset{108}{Ag} + \underset{63}{HNO_3} = \underset{170}{AgNO_3} + \underset{1}{H}$$

Using formula **6,** Art. **84,** *Theoretical Chemistry,*

$$z = \frac{m \times y}{a\,n},$$

and substituting the proper values, we obtain

$$z = \frac{108 \times 250}{170} = 158.82 \text{ g.} \quad \text{Ans.}$$

(63) $RhO$, $RhO_2$, $RhO_3$, and $Rh_2O_3$.

(64) See Art. **129.** $Ce_2O_3$ and $CeO_2$.

(65) See Art. **130.**

(66) $MnO_2$, manganese dioxide.
$Mn_3O_4$, red oxide of manganese.
$MnO$, manganous oxide.
$Mn_2O_3$, manganic oxide.
$MnO_3$, manganic anhydride.
$Mn_2O_7$, permanganic anhydride.

(67) (*a*) and (*b*) See Art. **178.**

(68) (1) $2PbS + 3O_2 = 2PbO + 2SO_2.$

(2) $PbS + 2O_2 = PbSO_4.$

(3) $PbS + 2PbO = 3Pb + SO_2.$

(4) $PbS + PbSO_4 = 2Pb + 2SO_2.$

(69) $$\underset{174}{2MnO_2} + \underset{48}{3O} + \underset{94}{K_2O} = \underset{316}{K_2Mn_2O_6}$$

Using formula **5,** Art. **84,** *Theoretical Chemistry,*

$$y = \frac{an \times z}{m},$$

and substituting the proper values, we obtain

$$y = \frac{316 \times 1{,}010}{174} = 1{,}834.25 \text{ g.} \quad \text{Ans.}$$

(70) See Art. **181.**

(71) See Art. **124.**

(72) $Au_2O$, $AuO$, and $Au_2O_3$.

(73) The specific gravity of platinum is 21.5 and that of nickel 8.6. From this data we obtain the proportion

$$21.5 : 8.6 = 392 : x,$$

or $$21.5 : 8.6 = 392 : 156.8,$$

from which it follows that a vessel of the same shape and size, made of nickel, would weigh 156.8 grams.

(74) See Art. **38.**

(75) In chromic oxide $Cr_2O_3$, chromium is a triad.
In chromium dioxide $CrO_2$, chromium is a tetrad.
In chromium trioxide $CrO_3$, chromium is a hexad.
In chromous oxide $CrO$, chromium is a dyad.

# INDEX.

NOTE.—All items in this index refer first to the section (see Preface, Vol. I) and then to the page of the section. Thus, "Combustion 5 86" means that combustion will be found on page 86 of section 5.